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THE OPTICAL REQUIREMENTS OF AIRPLANE MAPPING[1]

By I. C. Gardner

ABSTRACT

A definition of stereoscopic parallax is given and the relation between the stereoscopic parallax and the angular field of view of the airplane camera is derived. The stereoscopic parallax increases, to an important extent, as the field of view is increased. This makes the use of a large field of view, obtained by a wide angle lens or by a multiple lens camera, particularly desirable as it not only lessens the expense of flying, but increases the precision of the measurements obtained. In so far as the optical requirements are concerned, the required accuracy for the contours, together with the angular field of view, determines the necessary scale factor; and this, in turn, with the altitude of the airplane, determines the focal length of the objective which must be used in the airplane camera. The relations between the distortion and curvature of field of the camera objective and the resulting errors in the contours are considered. Measured values of the distortion of airplane photographs indicate that many of the photographic objectives in use are not sufficiently free from distortion to produce negatives satisfactory for topographic mapping. A large field of view and an increased freedom from distortion are of the greatest importance in extending the application of airplane photographs to the construction of topographic maps. If these characteristics can not be improved it may be desirable to develop a multiple lens camera having precision sufficient for topographic mapping and with a field of view, perhaps not so great as that of the present military multiple lens camera.

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I. INTRODUCTION

To increase the precision with which topographic maps[2] can be constructed from airplane photographs it is desirable that all sources of error be examined and their effect on the final map appraised. The precision of such maps may be limited by many causes, among which are defective imagery produced by the optical systems employed in exposing and measuring the negatives, inaccuracies in the measuring mechanism, film shrinkage, improper compensation of the tilt which the camera had at the time of the exposure, and the imperfect relative adjustment of the members of the successive pairs of negatives which are examined stereoscopically. In the present paper, however, all errors will be ignored except those which arise from the character of imagery registered upon the emulsion by the photographic lens used in the camera. An ideal limiting performance will be derived which can not be excelled by improvement in technique or in the mechanical

[1] An invited paper presented October 24, 1931, at the meeting of the Optical Society of America.
[2] Throughout this discussion the term "topographic map" will be understood to apply only to maps on which the elevation of all parts is indicated, either by contours or otherwise.

portions of the apparatus employed. Hope for greater precision must await further improvement of the photographic objective or of the photographic emulsion. On the other hand, the difference between present-day performance and this ideal limiting performance is a measure of the improvement which remains to be made in technique and apparatus if the full possibilities of the present photographic objectives are to be realized.

II. STEREOSCOPIC PARALLAX

When an exposure is made from an airplane, even though the camera is directed vertically downward, the resulting negative will not be a true horizontal projection or map of the region photographed if it deviates from a horizontal plane. Elevated points will be displaced outward from the center of the photograph and depressions will be drawn inward. This apparent displacement arises because the photograph is a projection on a plane from a point at a finite distance from the territory mapped. This is one of the difficulties which makes it impossible in many cases to construct a satisfactory map by the assemblage of separate photographs into a mosaic. When, however, topographic maps are to be made from airplane photographs this apparent displacement of elevated or depressed points not only ceases to be a detriment, but actually becomes the significant characteristic which makes topographic mapping possible.

The manner in which this apparent displacement of elevated or depressed points gives rise to stereoscopic parallax is illustrated by Figure 1. It will be assumed that AB represents the datum plane

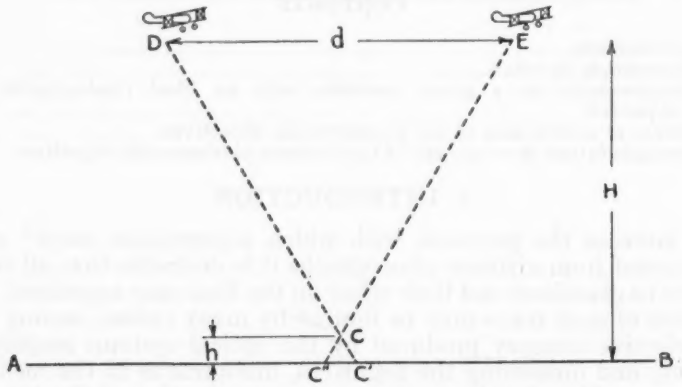

FIGURE 1.—*The derivation of stereoscopic parallax*

and that the point C lies h units above this plane. From the airplane two exposures are made, the first when the plane is at D and the second when it is at E. On the first negative the point C will be positioned as though it lay in the datum plane at C'. On the second negative it will appear to lie in the datum plane at C''. The relative displacement $C'\ C''$ will be termed the stereoscopic parallax. It is evident that the stereoscopic parallax may also be measured as an angular displacement or as a displacement on the negative, but, for the present purposes, it will be convenient to designate it as an apparent displacement measured in the datum plane. For all points common to

the pair of photographs and at a height h above the datum plane it is evident that the stereoscopic parallax has the same value for it is equal to

$$\frac{d\,h}{H-h} \tag{1}$$

where d is the distance from D to E and H is the height of the airplane when the two exposures are made. In a great number of cases, to a satisfactory degree of approximation, one may write

$$\text{Stereoscopic parallax} = h\frac{d}{H} \tag{2}$$

and, for moderate elevations, to an approximation satisfactory for the present purposes, it may be assumed that the stereoscopic parallax is proportional to the elevation of the point in question.

It is evident that the stereoscopic parallax of a point can not be measured unless the point appears on two different photographs. Consequently, if an airplane flies in a straight line, making exposures at regular intervals, it is essential that successive exposures overlap 50 per cent in order that the stereoscopic parallax of any desired point can be determined. Fifty per cent is the minimum overlap. As a matter of fact, it is desirable in all processes, and necessary in some, that a fair proportion of the points appear in three successive photographs. Consequently the nominal overlap is commonly 60 per cent. With this information the equation for the stereoscopic parallax may be advantageously modified. If the half-angular field of view of the camera, measured in the plane which includes the median of the photographic plate parallel to the direction of flight is α degrees, then $2H$ tan α is the distance, measured parallel to the travel of the plane, of two extreme points included in a single photograph. Consequently, if there is to be a 60 per cent overlap, d, the distance traveled between two successive exposures will be $0.8\ H$ tan α. Substituting this value of d in the approximate equation for the stereoscopic parallax, it becomes

$$\text{Stereoscopic parallax} = 0.8\ h \tan \alpha \tag{3}$$

With the definition of stereoscopic parallax which has been given, it will be noted that the stereoscopic parallax of a given point is proportional to its elevation and proportional to the angular field of view of the camera but is independent of the height of the plane. If all other conditions can be properly controlled it is evident that the precision can be improved by increasing α, the half-angular field of view of the camera. For the single-lens camera at present available the limit in this direction is soon reached at about 60° for 2α, but the multiple-lens camera is a means by which the value of α can be considerably increased. With a camera of this sort exposures are taken simultaneously from the airplane with 3, 5, or 9 lenses mounted in a fixed relation to each other. A knowledge of the angles between the axes of the different lenses enables the different photographs to be copied and rectified in such a way that they may be combined to form a single large photograph. If the rectification has been correctly done this single large photograph, except for the effects of aberrations and other secondary defects, shows the same perspective as though a single photograph had originally been taken with one

lens embracing all of the fields of view of the separate lenses. The outstanding advantage of the multiple-lens camera is that it enables an extremely large area to be reproduced according to a single perspective system.

As has already been mentioned, a second advantage of the multiple-lens camera lies in the great increase of the stereoscopic parallax by reason of the increased angular field of view. It would seem that the 9-lens camera should give a field of view having its angular diameter approximately three times that of the single-lens camera. However, there are several characteristics which prevent the use of such a large field for topographic work. In the process of rectification the peripheral portions of the picture are greatly enlarged and there is a corresponding loss of detail. These portions are also likely to be adversely affected by atmospheric haze because of the long light path. Furthermore, even if the negatives were sharply defined over the extremely large field, there is serious danger that the measurement of the stereoscopic parallax will be incorrectly made because of the greatly different aspects of the object points from the two widely separated view points. Then, too, inaccuracies in the rectification and assembly of the different exposures introduce errors. These various difficulties have prevented the use of the multiple-lens camera for precise topographic surveying. However, the larger field of view has the advantage of the greater stereoscopic parallax and, if the field of view of the single-lens camera can not be greatly increased, it seems not unreasonable to believe that economic conditions, in time, will justify the construction of multiple-lens cameras sufficiently precise for topographic work.

III. REQUIREMENTS FOR A GIVEN PRECISION WITH AN IDEAL PHOTOGRAPHIC OBJECTIVE

A most important portion of the equipment necessary for airplane surveying is the photographic emulsion, and some appraisal must be made of the precision with which the location of an image on a negative may be measured. The limit of resolution of a photographic film is of the order of 0.020 to 0.025 mm. In other words, a pair of lines separated this distance on a negative will be recorded as two lines just sufficiently distinct to permit a measurement to be made on each line. The probable error of a single setting on one of these lines will evidently be considerably less than the distance between the two lines. It will be assumed that the probable error of a single setting on a line is 0.004 mm which is one-fifth to one-sixth of the distance between two lines which are just resolved. This assumption is somewhat arbitrary but, if in error, it is believed that it under estimates the precision with which measurements of fairly well-defined images may be made on a photographic negative.[3] If the probable error of a single setting on a point is 0.004 mm, the probable error in the determination of a length by a single measurement at each end will be approximately 0.006 mm.

This selection of the probable error to be assumed is of fundamental importance for the entire discussion. In the laboratory, on photographs of test objects, it is not difficult to make measurements with a

[3] This uncertainty of measurement on the photographic emulsion arises from the grain of the developed image and does not include the errors introduced by film shrinkage. This latter type of error has not been included because we are here endeavoring to appraise an ideal best possible performance and film shrinkage can be eliminated by the use of glass plates.

precision considerably greater than that which has been here assumed. In airplane mapping, as practiced at present, the points on which observations are made are not always viewed against a background which provides conditions for the best definition. Furthermore, even with perfect lenses, the turbidity of the atmosphere introduces a loss of definition which tends to further increase the probable error of a setting. However, Edward H. Cahill, with Brock & Weymouth (Inc.), informs me that their operators on the stereoscopes can read the parallax of a point with a total variation of the order of 0.015 mm. As the pictures used in the stereoscope in the Brock process are magnified 2 diameters from the original negatives, this value does not differ greatly from that indicated by the assumption of a probable error of 0.006 mm on the original negative.

In order to have a concrete problem to which consideration can be directed it will be assumed that the allowable probable error in a contour is 1 foot (300 mm).[4] The stereoscopic parallax corresponding to a change of elevation of 300 mm is 240 tan α millimeters and, if this is to be the probable error of a single setting on the negative, the scale must be such that it corresponds to 0.006 mm on the plate; that is, the scale factor of the photograph must be equal to

$$\frac{0.006}{240 \tan \alpha} = \frac{1}{40{,}000 \tan \alpha} \text{ approximately} \qquad (4)$$

Before evaluating this expression further it is well to note a general conclusion which is apparent from this result. The scale factor required for a given precision is not a function of the height of the plane. Consequently if α, the half-angular field of view of the camera is held constant, the precision will be unaffected by the altitude of the plane, provided that objectives of different focal lengths are selected for the different altitudes in such a manner that the scale factor is unchanged. The advantage of the greater flying height and the objective of correspondingly longer focal length lies in the fact that fewer pictures are required for a given area and consequently the labor of securing the data from the negatives is greatly reduced.

The values of the ideal scale factors corresponding to several different values of the half-angular field of view have been computed from equation (4) and are given below:

Half-angular field of view $=\alpha$	Scale factor $= \frac{1}{40{,}000 \tan \alpha}$
25°	$\frac{1}{18,600}$
30°	$\frac{1}{23,000}$
50°	$\frac{1}{48,000}$
60°	$\frac{1}{69,000}$

When using these values it must not be forgotten that they are ideal values which, in their derivation, are based upon the assumption that

[4] Commercially used specifications for airplane topographic mapping have in some cases required that 90 per cent of the contours must not be in error by more than 50 per cent of the contour interval. For a contour interval of 10 feet this corresponds to a probable error of 2 feet instead of 1 foot as has been assumed in this discussion. For a 10-foot contour interval, therefore, the probable error assumed is smaller than has been found necessary for some commercial mapping.

all errors are eliminated except those introduced by the limited resolution of the photographic emulsion. The first two tabulated values may be considered as characteristic of single-lens cameras and the last two apply to multiple-lens cameras. For a probable error of 1 foot in the contours the smallest scale factor that would be used with a half-angular field of 30°, according to present commercial practice, is perhaps $\frac{1}{7,000}$ and probably, in most cases, a considerably larger scale factor would need to be employed to insure a probable error less than 1 foot over all parts of the map. This difference between $\frac{1}{23,000}$ and $\frac{1}{7,000}$ may be attributed, on the one hand, to the distortion and poor definition of the objective as will be shown in the following section and, on the other hand, to the several operations which intervene between the making of the exposure and the final production of the maps.

In making this comparison the discrepancy between theory and actual practice is perhaps even greater than is indicated, because the determination of the probable error of a single isolated point has been under consideration. Actually, however, measurements are taken on a very large number of points and the construction of the contours involves an averaging or smoothing process by which there is a considerable gain in precision. In deriving the scale factors tabulated above, this averaging effect has not been included and this omission tends to bring the tabulated theoretical values of the scale factor closer to the values in actual use.

IV. EFFECTS OF ABERRATIONS OF THE PHOTOGRAPHIC OBJECTIVE

In deriving the ideal scale factors which have been given as necessary for a certain precision, the consequences of the aberrations of the photographic objective have not been considered. Of these, the effects of distortion and the falling off in the quality of definition at the edge of the field are the most obvious. It is, of course, well known that the images of all points are displaced in a radial direction either toward or from the center of the field and, unfortunately, the magnitude of this displacement is often very large in comparison with the precision with which the location of a point on the negative can be determined. When making a mosaic, from photographs having an overlap of 50 or 60 per cent, this optical distortion is not particularly serious because only the central portion of each exposure need be utilized. When using the same series of negatives, however, for the construction of a topographic map, it is necessary that the marginal portions of the negatives be used and the distortion, if uncompensated, may easily be as great as the stereoscopic parallax from which the elevation of a point is to be determined. This distortion, by the lens, leads to systematic errors in the determined values of the elevation which can be compensated by the use of the proper corrections. However, the application of corrections is an added complication which introduces many difficulties and it is obviously desirable to have conditions such that the effect of the distortion may be neglected.

Some general considerations regarding the character of the distortion of a lens are now necessary. Analytically the distortion of a point may be expressed as a series of terms in α^3, α^5, etc., where α is the angular distance of the point from the center of the field; but, for points very near the center of the field, the distortion may be assumed to vary as α^3. If a lens is well corrected for distortion the higher order distortions will be balanced against the third order terms and the distortion over the central portion of the field will be negligible but for values of α greater than a given value the distortion will increase rapidly. For two lenses of the same design but differing in focal length, if the control during manufacture has been sufficiently exact, the distortions, for a given value of α, will vary directly as the two focal lengths. The Bureau of Standards has had occasion to test a large number of lenses destined for use in airplane photography by the different departments of the Government and by private firms. For the great majority of lenses tested the distortion, 25° from the axis, for a focal length of the order of 180 mm is as great as 0.1 mm. This is approximately twenty times the probable error of a single setting on a point on the negative. If exposures with such a lens are made from a height of 10,000 feet this distortion will introduce a systematic error at the edge of the field corresponding to a difference in elevation of approximately 15 feet. Most of these lenses were to be used for mapping, although probably not for topographic mapping. However, the results found from the tests of these lenses clearly indicate the need for such tests before lenses of commercial quality are used for topographic mapping.

The results of some of these tests are shown in the accompanying illustrations. Figure 2 shows the distortion found in three lenses nominally identical and of a type commonly used for airplane photography. Forty lenses of this type submitted in a single lot were tested and the curves are typical of the amount of variation which was found. Figure 3 shows the freedom from distortion of a lens selected for topographic mapping purposes. The distortion in Figure 4 is characteristic of a lens which has been specially designed for airplane mapping and which regularly shows excellent freedom from distortion. Figure 5 shows the distortion curves for a lot of 10 lenses, nominally identical. For all the lenses of this group the distortion is small and the uniformity of product is rather remarkable.

The systematic errors introduced by the distortion shown for some of these lenses would largely destroy the usefulness of the resulting negative for topographic purposes. There are methods by which the detrimental effects of the distortion may be reduced. If pictures to the same scale are taken from a lesser altitude, as has been shown, the stereoscopic parallax will remain the same. However, if the scale is held constant, a lens of shorter focal length will have been used and the distortion will have been decreased in the same ratio as the altitude of the plane. Consequently the net result is a lessening of the effect of the distortion. On the other hand, if the original focal length and altitude are retained the overlap may be increased. With the increased overlap the value of the stereoscopic parallax decreases, but the corresponding decrease in the distortion is greater proportionately so that there is a lessening of the errors which it introduces. Each of these methods for improving conditions carries the disadvantage that an increased number of exposures are

necessary with a greatly increased cost in making the measurements on the plates. It should, perhaps, be mentioned that increasing the focal length of the objective in order to increase the scale of the picture does not, in itself, lessen the error introduced by distortion. If, for example, the focal length of the objective is doubled, the distance on the plate corresponding to the stereoscopic parallax for 1 foot is doubled. But if the type and quality of the lens remain the same the distortion is also doubled so that there is no net gain.

Aside from the systematic errors introduced by distortion there are accidental errors which arise from the failure to secure critical definition in the marginal portions of the plate because of the presence of curvature of field, astigmatism, or coma. For pictorial purposes the definition yielded by a modern lens appears to be satisfactory

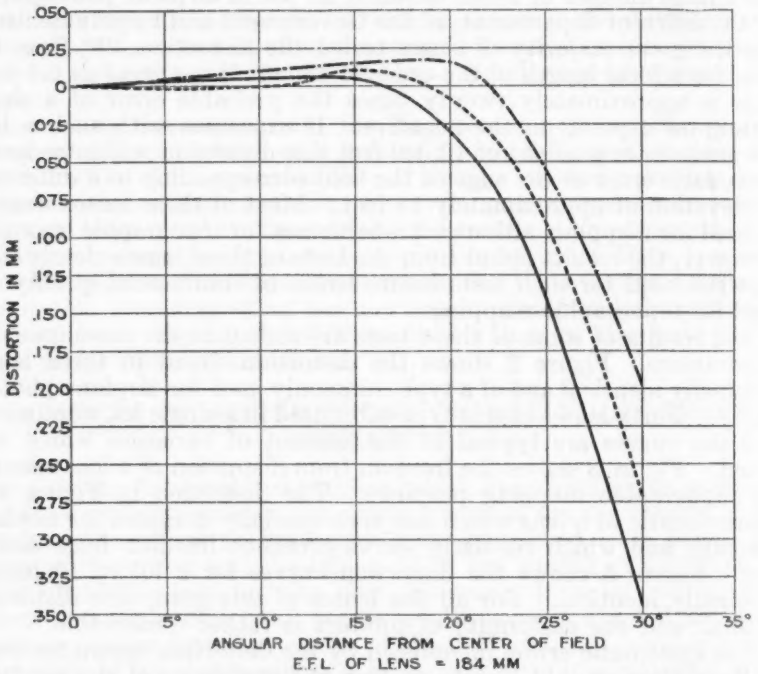

FIGURE 2.—*Distortion curves of three lenses which were nominally identical*

over all parts of the field. When, however, measurements of the resolving power are made for different portions of the field it is found that the boundary portions of the plate are not nearly so well defined as the central portions. Such a defect does not introduce systematic errors, but does greatly increase the accidental errors of observation. The difficulties of this nature are less important than those introduced by distortion because of this accidental character. Furthermore when contours are plotted the smoothing process, to which reference has already been made, tends to eliminate a portion of the errors of an accidental nature.

The extent to which the systematic errors arising from distortion and the accidental errors arising from impairment of the definition for the marginal portions of the field are to be tolerated is, to a

large extent, determined by the magnitude of the errors which are incident to the mechanism and methods by which the data are obtained from the negative. It appears that the errors of this sort which are made in measuring the negative are of the order of 0.015 to 0.030 mm. Such errors clearly demand that the distortion of the lens, for the portion of the field that is utilized, should be very much less than the 0.1 mm which has been previously discussed in connection with the consideration of distortion. Furthermore, if the errors of 0.015 to 0.030 mm are assumed to represent the errors which arise from defects in the measuring mechanism, the effects of these errors can be still further reduced if the measurements are made, not on the original negative, but on an enlarged copy. Of course it is necessary

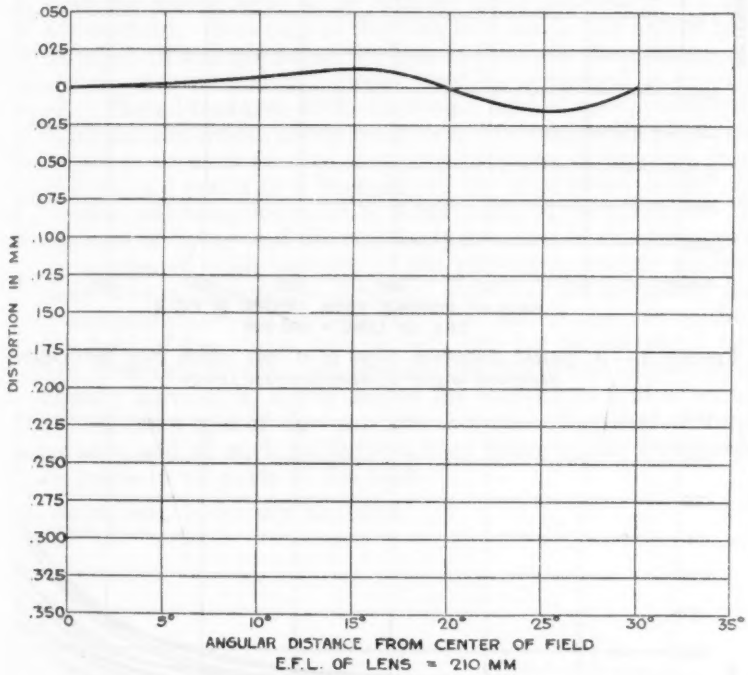

FIGURE 3.—*Distortion curve of a lens relatively free from distortion*
This particular lens was obtained by selection.

that the distortion introduced by the optical system of the enlarger be nil or, better yet, that it be so determined as to compensate the distortion of the original negative. The making of an enlarged copy on which the measurements are made is a practicable expedient which occupies a fundamental position in one commercial mapping process.

V. PROBABLE FUTURE DEVELOPMENT OF THE AIRPLANE PHOTOGRAPHIC OBJECTIVE

The scale factor found necessary in practice has been found in Section III to be approximately 3½ times that indicated by theory. When it is considered that this ratio is partially accounted for by the distortion and lack of perfect definition of the objective, this indicates that the mechanical equipment has been brought to such perfection

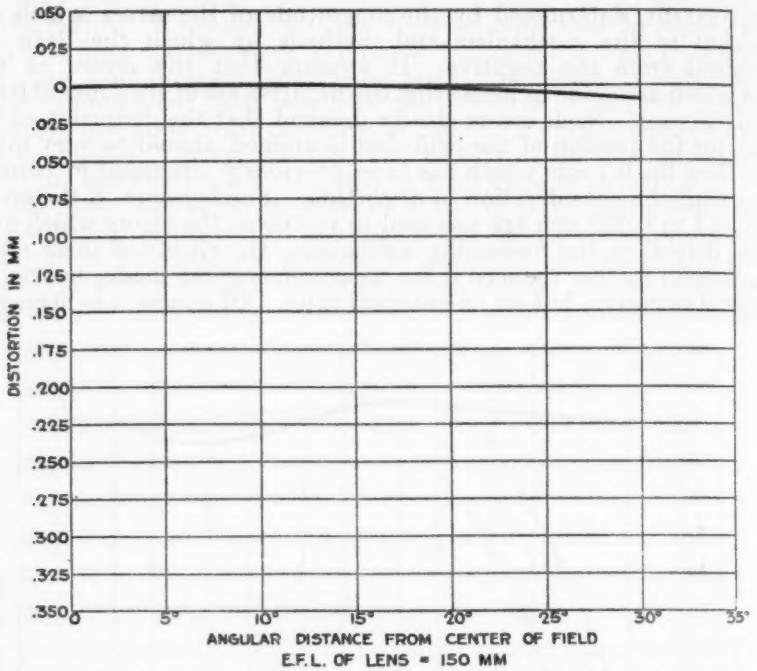

FIGURE 4.—*A typical distortion curve of a lens which was particularly designed to give a distortion-free image*

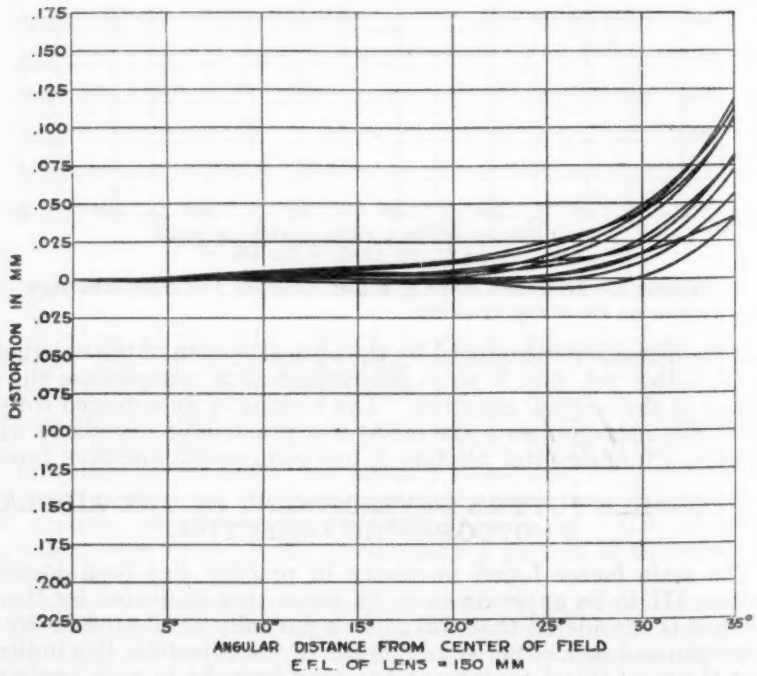

FIGURE 5.—*Distortion curves of 10 lenses which were nominally identical*

that it is fairly commensurate with the possibilities of the negatives taken with the photographic objectives and cameras which are at present available. It is obvious, upon a superficial examination, that one desires the largest possible field of view and the maximum freedom from distortion. However, by this consideration of errors, in which those arising from mechanical sources are purposely treated as absent, the requirements of the photographic objective are brought into strong relief. An increase in the useful field of view of the lens can only be brought about by an improvement in the correction for distortion because an enlarged field, over which definition may be entirely satisfactory for pictorial purposes, is quite useless for mapping unless the increased field is obtained without an increase in the linear value of the distortion on the negative. Furthermore it is important to note that the advantages to be derived from increasing the field of view are twofold. Not only is there an increase in the extent of territory included on a single negative, but, at the same time, the precision with which the vertical dimension may be measured is greatly increased. The advantages of the increased field of view, provided that it be free from distortion, are so great that is seems justifiable, certainly with lenses to be used on civil mapping projects, to increase the field even if it should result in a lessening of the true speed, either by the use of additional components or by a reduction in the aperture. When the high cost of flying and the relatively low cost of the photographic lens, as compared with the rest of the photogrammetric equipment, are taken into consideration, it seems also that the increased field of view is demanded, even at considerable increase in the cost of the lens.

If the field of the single lens camera can not be increased then it would be desirable to develop a precision multiple lens camera in which the primary purpose is, not to secure the maximum field of view, but rather to secure a field of view considerably exceeding that of the single lens camera and of such perfection that topographic measurements may be made in all parts of the field.

WASHINGTON, February 13, 1932.

NOTE ON THE MOVING BOUNDARY METHOD FOR MEASURING TRANSFERENCE NUMBERS

A PYCNOMETER FOR DETERMINING THE VOLUME CHANGE OCCURRING AT AN ELECTRODE AND ITS APPLICATION TO A CATHODE OF SILVER CHLORIDE IN A SOLUTION OF POTASSIUM CHLORIDE

By E. R. Smith

ABSTRACT

Transference numbers, measured by the moving boundary method, must be corrected for the change in volume which occurs at the electrode on the closed side of the transference cell. It has been customary to compute this volume correction from the densities of the electrode materials and of the solution, together with a value for the transference number. A method for measuring the volume correction is described. Measurements of the correction to be applied in the case of a silver-silver chloride electrode in potassium chloride solution show that the computed value is correct up to concentrations of 0.2 molal, to within the precision required.

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I. NOTATION

Δn_w, moles of water transferred from anode to cathode portion, per faraday.
T_x, "true" transference number of the ion x.
N_x, "Hittorf" transference number of the ion x.
r, ratio of moles of salt to moles of water in the original solution.
D, density of the original solution.
V, volume.
$\overline{V}_s$, partial molal volume of salt in the solution.
$\overline{V}_w$, partial molal volume of water in the solution.
ΔV_e, volume change of the electrode material, per faraday.
M_x, weight of one equivalent of ion x.
M = weight of one equivalent of salt.
Δm, change in total weight of the cathode tube and solution, per faraday.

II. INTRODUCTION

The volume change which occurs when electricity is passed across the junction between an electrode and an electrolytic solution is, in general, the result of several factors. Faraday's law governs the change in state at the electrode proper, while in the solution, the ions move in accordance with the phenomenon of transference. Consider,

for example, a cathode of silver coated with silver chloride and immersed in a solution of potassium chloride. When 1 faraday of electricity is passed from the solution to the electrode, one equivalent of solid silver chloride having a volume of V_{AgCl} disappears, one equivalent of solid silver having a volume of V_{Ag} appears, the amount of salt in the cathode portion is increased by T_K equivalents and the amount of water is increased by Δn_w moles. The volume change at the cathode is the resultant of all these effects and is therefore given by the equation

$$\Delta V = (V_{Ag} - V_{AgCl}) + T_K \overline{V}_s + \Delta n_w \overline{V}_w \quad (1)$$

in which $\overline{V}_s$ and $\overline{V}_w$ are the partial molal volumes of salt and water, respectively. It was first shown by G. N. Lewis [1] that the moving boundary method of measuring transference numbers gives the Hittorf number when the proper correction is made for the volume changes at the electrodes. The volume correction to be made in order to obtain the Hittorf number, as Lewis showed, is not the sum of all the terms comprising ΔV in equation (1), but is the sum

$$V_{Ag} - V_{AgCl} + N_K \overline{V}_s \text{ or } \Delta V_e + N_K \overline{V}_s \quad (2)$$

This volume correction can easily be calculated from density data, but with no assurance that the value so calculated is correct. Thus, from density values in International Critical Tables, $\Delta V_e = 10.3 - 25.8 = -15.5$ cm^3, from the tabulation of partial molal volumes by V. K. Lamer and T. H. Gronwall,[2] $\overline{V}_s = 27.81$ cm^3 for 0.2 molal potassium chloride solution, and from the precise measurements of D. A. MacInnes and M. Dole,[3] $N_K = 0.4897$ at 25°. The volume correction is therefore computed to be -1.9 cm^3, the negative sign denoting a decrease in volume at this electrode. However, it is well known that the densities of solids vary somewhat according to their physical state. The density of silver has been reported at values between about 9.8 and 10.6 and of silver chloride between 5.46 and 5.56, depending on the method of preparation and physical treatment.[4] Furthermore, at a silver-chloride cathode in potassium chloride solution, the increase in concentration of the solution occurs locally at the surface and in the pores of the silver chloride electrode. Since the transference number of potassium chloride is practically the same at all concentrations,[5 6] there is no tendency for the concentrated portion produced at the electrode to distribute by electrolytic migration, for the same number of ions of each kind migrate in or out of any portion of the solution. Consequently, except for the influences of gravity, diffusion and convection, a more and more concentrated solution surrounds the silver-chloride cathode as the electrolysis progresses. In addition to the slight change in partial molal volume of the salt with increase in concentration, it is quite possible that some silver chloride dissolves in the concentrated solution formed in the pores of the cathode and produces an added change in volume.

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[1] G. N. Lewis, J. Am. Chem. Soc., vol. 32, p. 862, 1910.
[2] V. K. Lamer and T. H. Gronwall, J. Phys. Chem., vol. 31, p. 393, 1927.
[3] D. A. MacInnes and M. Dole, J. Am. Chem. Soc., vol. 53, p. 1357, 1931.
[4] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 3, pp. 323 and 393; Longmans, Green & Co., London, 1923.
[5] E. R. Smith, B. S. Jour. Research, vol. 6, p. 917, 1931.
[6] See footnote 3.

In view of these uncertainties in the calculated volume corrections for moving boundary determinations, especially for junctions between solutions of the same salt at different concentrations where the correction may be of the same order of magnitude as the motion observed,[7] it appeared desirable to attempt the direct measurement of these volume corrections for comparison with the computed values.

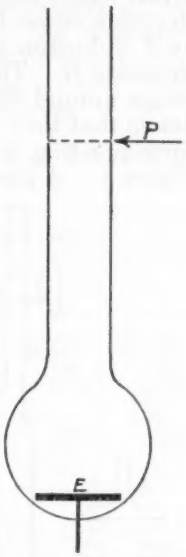

FIGURE 1.—*Removable electrode portion*

III. THEORY OF THE METHOD

Consider an electrode portion which can be separated from the remainder of the cell, by a method such as described in the next section, at a fixed plane P on the cell. (Fig. 1.) All of the concentration and chemical changes due to transference and the electrode reaction take place at the electrode E below the plane P. The resultant volume change around the electrode forces an equal volume of the unchanged middle portion of the solution in or out of the removable electrode portion; that is, past the plane P. At the same time, if E is a cathode, cations move into the portion and anions move out and, since the ions are hydrated, water will also be transferred past P. The change in weight of the electrode portion after the passage of one faraday will therefore be

$$\Delta m = M_c T_c - M_a T_a + 18.016\Delta n_w - (\Delta V_e + \overline{V}_s T_c + \overline{V}_w \Delta n_w)D \qquad (3)$$

The true transference numbers can be expressed in terms of the Hittorf numbers by the relations.[8]

$$T_c = N_c + r\Delta n_w \text{ and } T_a = 1 - N_c - r\Delta n_w \qquad (4)$$

Making this substitution and noting that $M = M_c + M_a$, we obtain the equation

$$\Delta m = MN_c - M_a - (\Delta V_e + \overline{V}_s N_c)D + \Delta n_w[18.016 + Mr - (\overline{V}_w + \overline{V}_s r)D] \qquad (5)$$

For dilute solutions, in the case of the alkali chlorides below about 0.5 molal,

$$18.016 + Mr - D(\overline{V}_w + \overline{V}_s r) = 0.000 \qquad (6)$$

and hence

$$(\Delta V_e + N_c \overline{V}_s) = \frac{MN_c - M_a - \Delta m}{D} \qquad (7)$$

From equation (7) it is seen that the desired volume correction, $(\Delta V_e + N_c \overline{V}_s)$, can be obtained by measuring Δm for a solution for which the density and Hittorf transference number are known.[9]

[7] See footnote 5, p. 458.
[8] E. W. Washburn, Principles of Physical Chemistry, p. 233, McGraw-Hill Book Co., New York, 1914.
[9] It is interesting to note that equation (5) may be used for the determination of Δn_w in any case where equation (6) can be evaluated, if the volume changes are known.

IV. APPARATUS

The pyrex glass cell, shown in Figure 2, was made in two parts which fitted together by means of the ground glass joint *E*. The electrode vessel *B* was essentially a pycnometer, of the type described by J. Johnston and L. H. Adams, [10] containing a sealed-in tungsten electrode *D*. The under side of the circular cap *A* and the top of the flange around the opening of *B* were ground and polished optically flat so that they made a precise fit for the pycnometer measurements, corresponding to separating the electrode portion at the plane *P* of Figure 1. A piece of platinum gauze was fitted on the tungsten wire and fastened in place by electroplating with a heavy deposit of silver. It was then coated electrolytically with chloride and covered with a layer of precipitated silver chloride *C*, prepared as described by Washburn.[11] The tube and stopcock *F* permitted the insertion of a pipet for the removal of a middle portion of the solution for analysis after an electrolysis.

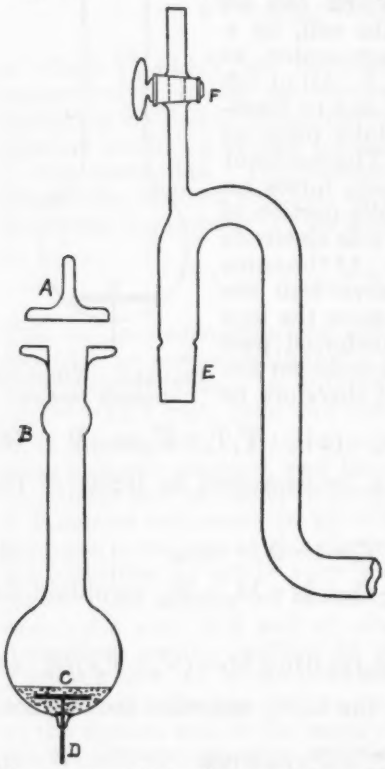

FIGURE 2.—*Electrode pycnometer and connecting portion*

Before electrolysis, the electrode pycnometer was filled with solution and immersed in a thermostat containing distilled water, an electrical heater, a motor-driven stirrer and a mercury regulator, the latter connected with a vibrator and an electron tube circuit for sensitive regulation. The temperature was held constant to within 0.01°. After allowing a half hour for the attainment of temperature equilibrium, the cap *A* was slid into place with a slight rotary motion, shearing off the projecting small portion of the solution. The tube was then removed from the thermostat, dried and weighed. The cap *A* was next removed and the whole cell fitted together by the ground joint *E*. The electrolyses were carried out over night at room temperature with a current of about 30 milliamperes. A small copper coulometer was used to measure the amount of electricity. After electrolysis, a middle portion was pipetted out for analysis, the cell separated into its two parts, and the pycnometer tube again brought to 25° in the thermostat, dried and weighed as before.

The potassium chloride was prepared by recrystallizing the c. p. salt, drying and heating to incipient fusion in a platinum dish. The solutions were prepared by weighing out the requisite quantities of salt and water.

[10] J. Johnston and L. H. Adams, J. Am. Chem. Soc., vol. 34, p. 563, 1912.
[11] E. W. Washburn, J. Am. Chem. Soc., vol. 31, p. 331, 1909.

V. EXPERIMENTAL RESULTS

It has not yet been found possible to get accurate transference numbers by the moving boundary method at concentrations above about 0.2 molal[3]. This concentration was chosen for the measurements on the silver-silver chloride electrode since if disturbing effects, such as the dissolving of silver chloride in the solution, occur they would be more apparent in the more concentrated solutions.

TABLE 1.—*The volume change at a silver-chloride cathode in 0.2 molal KCl solution at 25°*

	Experiment No.		
	1	2	3
Weight of electrode tube and solution before electrolysis	140.0662	139.7643	139.6352
Weight of electrode tube and solution after electrolysis	140.1382	139.8374	139.7037
Weight of Cu deposited in coulometer	.8885	.7888	.7751
Number of faradays	.02795	.02482	.02439
Δm	2.58	2.95	2.81
Composition of the original solution. g KCl/g solution	.01469	.01469	.01470
Composition of the middle portion. g KCl/g solution	.01468	.01467	.01474
$\Delta V_e + N_c \overline{V}_s$	−1.52	−1.89	−1.75

The experimental results are shown in Table 1. The average of the three measured values of $(\Delta V_e + N_c\overline{V}_s)$ is -1.7_2 as compared with the calculated value of -1.9 cm^3. Considering that both the measured and calculated value are uncertain in the second significant figure, the agreement is good. The equation for the correction of a moving boundary transference number is

$$N_c = N'_c \pm (\Delta V_e + N_c\overline{V}_2)C$$

in which N'_c is the uncorrected value of the transference number and C is the concentration of the solution expressed in equivalents per cubic centimeter. For example, the measured value of N'_c in one experiment [12] was 0.4904 for 0.2 molal potassium chloride, in which $C = 0.1983 \times 10^{-3}$, with the use of a silver chloride cathode at the closed side of the cell. The measured correction to be applied is therefore $-1.7 \times 0.1983 \times 10^{-3} = -0.00034$ and the calculated correction is $-1.9 \times 0.1983 \times 10^{-3} = -0.00037$. The corrected value of the transference number is therefore 0.4900_6 or 0.4900_3, respectively. The difference is outside the precision of the measurement of transference numbers and leads to the conclusion that the computed corrections may be applied with confidence in the case of potassium chloride solutions up to 0.2 molal.

The author desires to express appreciation to E. W. Washburn, for suggesting the design of apparatus and the method used in this research and for helpful advice and interest during the course of the measurements.

WASHINGTON, January 21, 1932.

[12] E. R. Smith and D. A. MacInnes, J. Am. Chem. Soc., vol. 47, p. 1013, 1925.

FIELD-INTENSITY MEASUREMENTS AT FREQUENCIES FROM 285 TO 5,400 KILOCYCLES PER SECOND

By S. S. Kirby and K. A. Norton

ABSTRACT

Radio field intensities were measured at distances of only a few wave lengths from a transmitting station on a wide range of frequencies, including the broadcast band, in order to determine the distance at which ground absorption became appreciable. At a distance of 2.4 km, there was no appreciable absorption for frequencies below about 1,000 kc; above this frequency, the absorption became appreciable and increased as the frequency was increased. Daylight measurements made at greater distances on broadcast transmissions, airways phones and airways beacons show that field intensities fall off to 1 per cent of what the inverse distance law with no absorption would give at distances from 100 to 400 km, depending on the frequency and the nature of the ground. The experimental data were compared with Rolf's attentuation graphs in order to determine the electrical constants of the land east and west of the Allegheny Mountains. East of and including the mountains (Maryland, Pennsylvania, and New Jersey) the conductivity and dielectric constant were found to be 3.35×10^{-14} e.m.u. and 13, respectively; west of the mountains (near Chicago) they were found to be 1.07×10^{-13} e.m.u. and 13, respectively. Using these constants theoretical values of field intensity were graphed for these two types of ground and for broadcasting frequencies.

The experimental data were also compared with results given by the Austin-Cohen transmission formula. It was found that for overland transmission in the range of frequencies observed this formula did not satisfactorily give the variations in field intensity as the distance was changed or as the frequency was changed.

The measurements reported in this paper are part of a research on the accuracy of means of measurement of radio field intensity. Measurements of received field intensities at broadcasting frequencies, at a distance of about 3 km from a radio transmitting station, were compared with values calculated from the simple radio transmission formula. Let F_m represent the measured value of field intensity and F_c the value calculated from the simple transmission formula in which the earth is assumed to be perfectly conducting. It was found that the ratio $\frac{F_m}{F_c}$ decreased at this distance as the frequency increased. The transmission formula used was the familiar inverse distance formula

$$F_c=\frac{377\,h\,f\,I}{c\,d}\text{ volts/cm} \qquad (1)$$

where

h = the effective height of transmitting antenna in centimeters.
f = the frequency in cycles per second.
I = current in transmitting antenna measured in amperes.
c = velocity of propagation of electromagnetic waves (3×10^{10} cm/sec.)
d = distance in centimeters from transmitter to the point at which the field intensity was measured.

The field intensities were measured with a commercial field intensity measuring set, which had been checked against measuring sets constructed by the bureau. The transmitting antenna used was a condenser antenna 114 cm high and 750 cm radius. The value used for h was the actual distance between the plates of this arrangement. The transmission path was almost entirely over river water, the transmitting and receiving stations being located on opposite shores of the Potomac River. The fact that the ratio F_m/F_e decreased as the frequency increased was interpreted to mean that there was an appreciable absorption at these frequencies over even this short path. These observations were checked with a vertical wire antenna and a loop antenna with similar results.

In order to check the conclusion that absorption was appreciable over distances of a few kilometers at broadcast frequencies the field

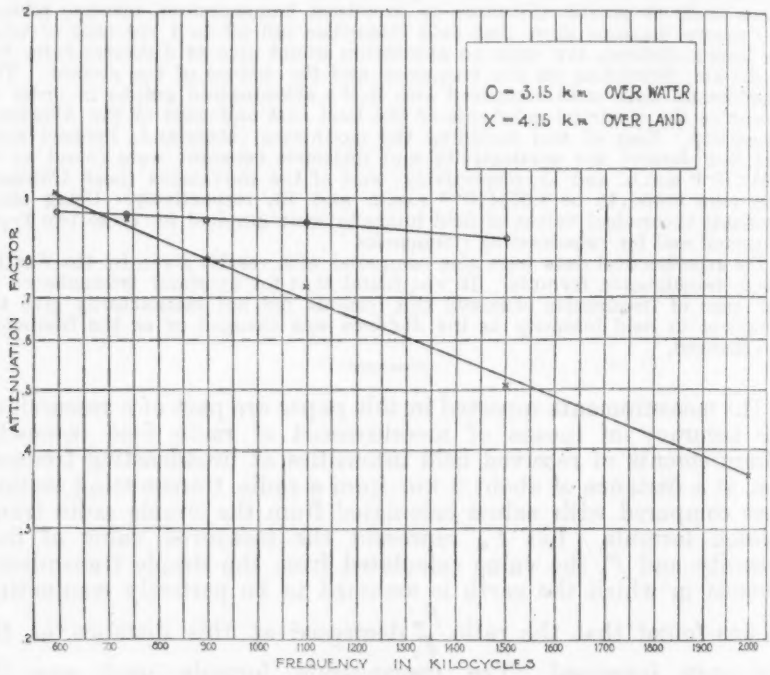

FIGURE 1.—*Attenuation factors versus frequency*

(The upper one for d=3.15 km over fresh water and the lower one for d=4.15 km over land.)

intensity measuring set was put on a boat so that its distance from the transmitter could be varied in a straight line and so as to obtain uniform ground conditions. The transmitter was set at the water's edge at low tide and was over water at high tide. A loop antenna was used with the transmitter in this case. Measurements were made at distances of 1 to 2 wave lengths and at the distance of 3.15 km (corresponding to 5 to 16 wave lengths) from the transmitting station. The ratio of F_m/F_e at the greater distance was divided by that ratio at the nearer distance to get the "attenuation factor" A which we define as

$$A=\frac{F d}{F_1 d_1} \tag{2}$$

where F_1 is the field intensity measured at a distance d_1 kilometers which is so near the transmitter that absorption has not yet become appreciable, and F is the measured field intensity at any greater distance d kilometers. All conditions at the transmitter (that is, antenna current, tide, frequency, etc.) are the same when these two measurements are made. The results of these measurements are shown by the upper graph of Figure 1. The lower graph of Figure 1 shows attenuation factors obtained in a similar manner over a land path of 4.15 km.

The ratios of F_m/F_c (not A) were also determined for eight different distances over the water path and for several different frequencies from 590 to 5,400 kc. The results of these measurements are shown in Figure 2. For frequencies up to 1,100 kc no appreciable absorption could be detected at distances up to 2.4 km. The accuracy of the measurements was about 5 per cent and ratios differing from unity by

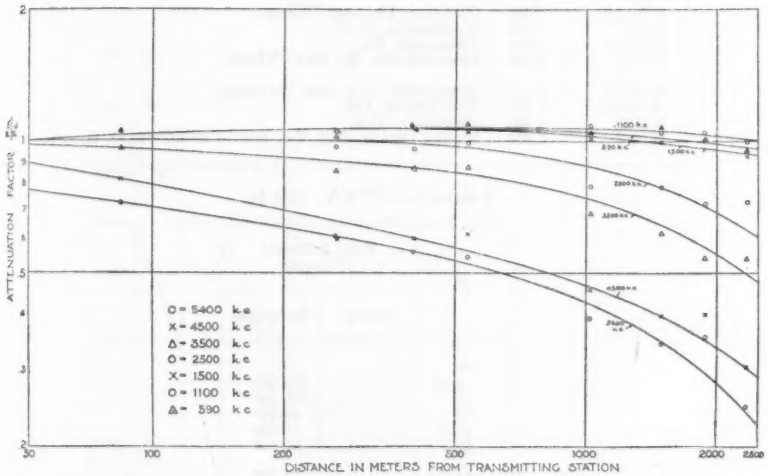
ATTENUATION FACTOR
DISTANCE IN METERS FROM TRANSMITTING STATION
O = 5400 kc
X = 4500 kc
Δ = 3500 kc
O = 2500 kc
X = 1500 kc
O = 1100 kc
Δ = 590 kc

FIGURE 2.—*Attenuation factor F_m/F_c versus distance for various frequencies with a water path*

(Graphs are not theoretical as are some of the later graphs.)

less than this amount indicated no appreciable absorption. At higher frequencies the absorption became appreciable and increased as the frequency increased.

The results of these two experiments showed that if field intensity measurements were made around a transmitting station to determine the actual radiation, they should be made fairly close to the transmitter, say within 5 wave lengths, for frequencies in the broadcast band, in order to avoid errors due to absorption. The maximum distances at which such measurements should be made depend on the nature of the transmission path. Over highly conducting ground such measurements could be made farther from the transmitting station than over poorly conducting ground.

Later daytime field intensity measurements were made of transmissions from 12 broadcasting stations, 3 airways phones, 1 airways radio range beacon, and the Bureau of Standards experimental beacon, at various distances, from 1 to 3 km out to several hundred kilometers from the transmitting station. Usually the near-by measurements

were taken within the distance at which absorption began as was determined by Figures 1 and 2. Two trips were made with a field intensity measuring set in a laboratory truck. The first trip was made June 2 to 7, 1930, over path No. 1 as shown in Figure 3. The second trip was made November 3 to 19, 1930, over paths 2, 3, and 4. The stations measured were:

Station	Frequency	Location
	kc	
WWV	290	College Park, Md., near Washington.
WWU	338	New Brunswick, N. J.
WWO	344	Cleveland, Ohio.
KDA	350	Maywood, Ill., near Chicago.
WMAL	630	Washington, D. C.
WMAQ	670	Addison, Ill., near Chicago.
WGN	720	Elgin, Ill.
WJZ	760	Bound Brook, N. J.
WBBM	770	Glenview, Ill., near Chicago.
WRC	950	Washington, D. C.
KDKA	980	Pittsburgh, Pa.
KYW	1,020	Bloomingdale, Ill., near Chicago.
WTAM	1,070	Brecksville, Ohio, near Cleveland.
WOWO	1,160	Fort Wayne, Ind.
WHK	1,390	Cleveland, Ohio.
WJSV	1,460	Mount Vernon Hills, Va., near Washington, D. C.

TABLE 1.—*WGN, 720 kc*

D	Field intensity μV/meter	
	Going	Returning
km		
3.86	----------	356,000
13	----------	124,900
29	----------	49,950
36.5	----------	34,000
45.7	----------	25,200
61.5	----------	14,595
78.5	8,650	8,720
92.0	----------	7,140
109.3	4,275	4,010
131	----------	1,854
150	1,192	1,269
192.5	600	614
243	317.5	318
281	237.0	230
326	183.9	184
375	146.1	155
414	89.5	87.8
456	61.9	61.1
492	54.7	----------
496	----------	36.7
513	----------	43.4
532	----------	23.4
595	----------	9.6

The field-intensity measurements made on these trips are plotted on Figures 4 to 10, inclusive. In order to give some idea of the variations in the field intensities from day to day the measurements made on station WGN are listed in Table 1. It may be seen that the measurements on the trip into Chicago agree very well with those made on the trip out of Chicago. It may be of some interest to men-

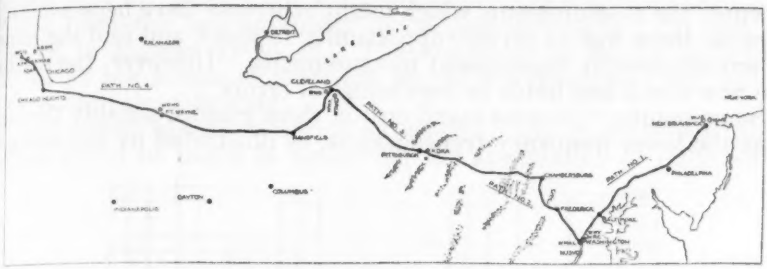

FIGURE 3.—*Paths over which field-intensity measurements were made of transmissions from broadcasting and airways stations*

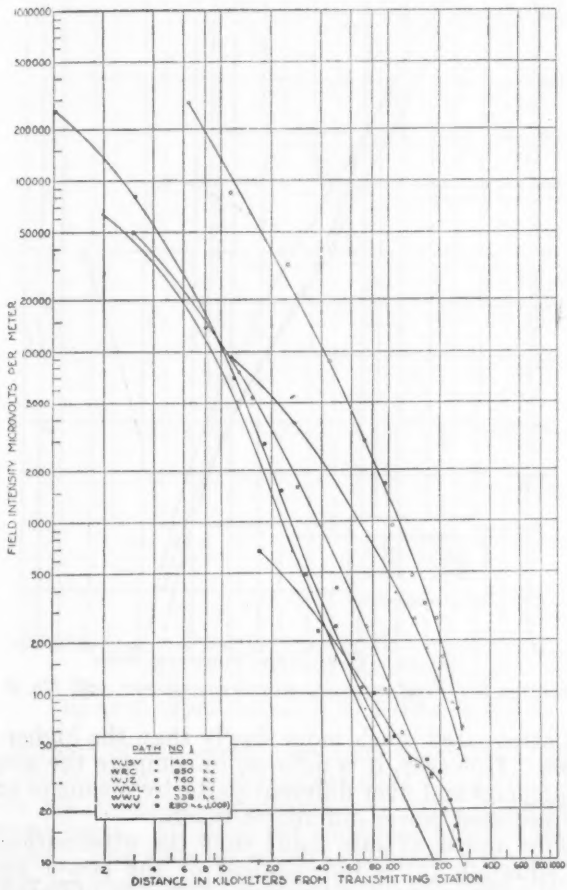

FIGURE 4.—*Field-intensity measurement over path No. 1*

tion at this point that the field intensities were not calculated from the data until the trip was finished. This allowed some irregularities to enter the measurements which might otherwise have been avoided, because there was no further opportunity to check and find the cause of any apparently inconsistent measurements. However, the results are now much less liable to psychological errors.

Some points of interest stand out on these graphs, notably the fact that the lower frequency transmissions, as illustrated by the airways

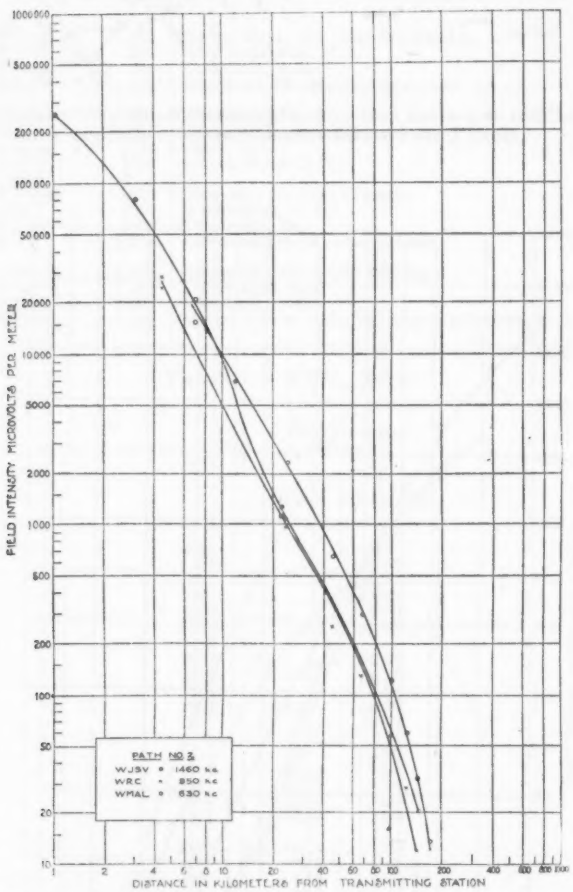

FIGURE 5.—*Field-intensity measurements over path No. 2*

phones, are attenuated much more slowly than the higher frequency transmissions. However, it is difficult to compare the absorption at various frequencies and over different paths by means of such graphs because the radiated power differed so much.

It should be noted at this point that the attenuation factor as defined by equation (2) is independent of the power used by the transmitting station provided the same power is radiated when the measurement at d is made as when the measurement at d_1 is made. The stations measured usually maintained their antenna current at a fairly constant value during the measurements and consequently

the values of A may be considered to represent the average characteristics of a radio-transmission path for any given frequency. These values of A for most of the experimental results described are determined from the measurements by means of equation (2) and are plotted in Figures 11 to 16. The experimental results are represented by the points plotted; the graphs are theoretical and will be discussed in the following:

In the past various attempts have been made to develop a theory which would be useful in predicting the attenuation of radio waves

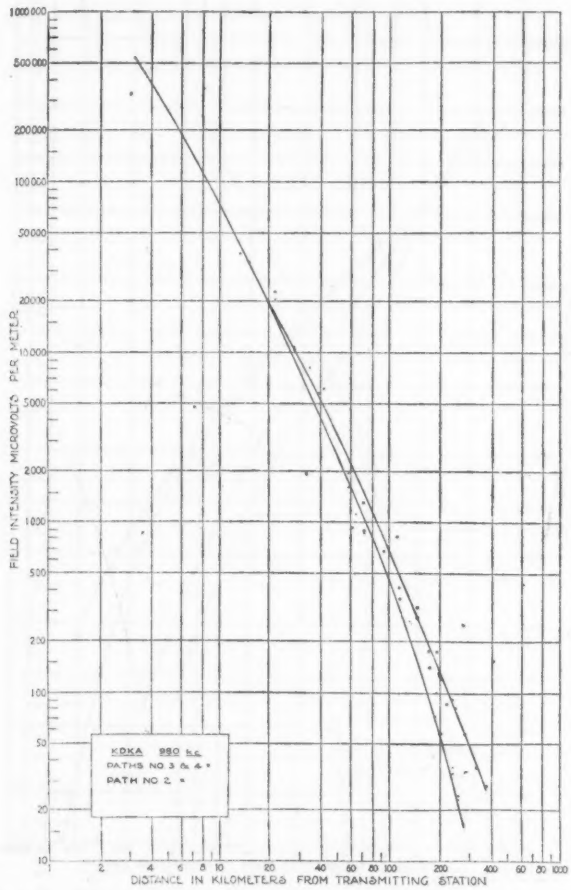

FIGURE 6.—*Field intensities for KDKA on 980 kc*

along the surface of the earth. In 1909 Sommerfeld published his paper The Propagation of Waves in Wireless Telegraphy.[1] However, the analysis was quite involved and very little use was made of it until in recent years. In 1911, the empirical Austin-Cohen formula [2] was published. The data on which it is based were obtained in the daytime over sea water and for frequencies less than 1,000 kc and for

[1] Ann. d. Physik (4), vol. 28, pp. 665 to 736, 1909.
[2] L. W. Austin, Some Quantitative Experiments in Long Distance Radiotelegraphy, B. S. Sci. Paper No. 159. B. S. Bull., vol. 7, No. 3, p. 315, 1911.

distances up to 1,900 km. Since it was published it has been used quite extensively for over land as well as over water paths and over a wide range of frequencies and distances. It should be emphasized that many of these conditions were far different from those for which the Austin-Cohen formula was derived. No evidence which contradicts this formula for the conditions under which it was derived is presented in this paper. We do, however, present data which show that this formula is not usable for overland transmissions at broad-

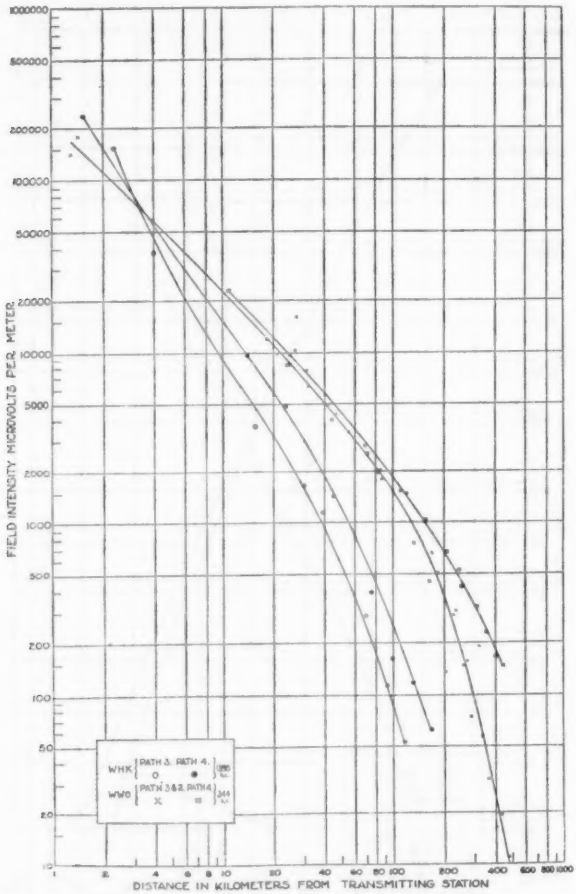

FIGURE 7.—*Field-intensity measurements for paths Nos. 3 and 4*

cast frequencies. Our data also indicate that, in the absence of downcoming waves, the Sommerfeld theory represents the facts fairly well.

In the Austin-Cohen formula the attenuation factor is given by

$$A = e^{-\alpha\sqrt{f}D} \tag{3}$$

f = frequency in kilocycles per second.
D = distance from transmitting station in kilometers.

If a formula of this type correctly represented the law of decay, it would be possible to determine an α for any given radio-transmission path (supposed electromagnetically homogeneous) which would then determine the proper attenuation factors at any point of the path and for any frequency. From our experimentally determined values of A (see equation (2)), a value of α is determined for each measurement made by substituting in equation (3). The values of α so determined for the measurements on path No. 1 are given in Table 2. These values are then averaged giving a value of $\alpha = 0.00116$, which should

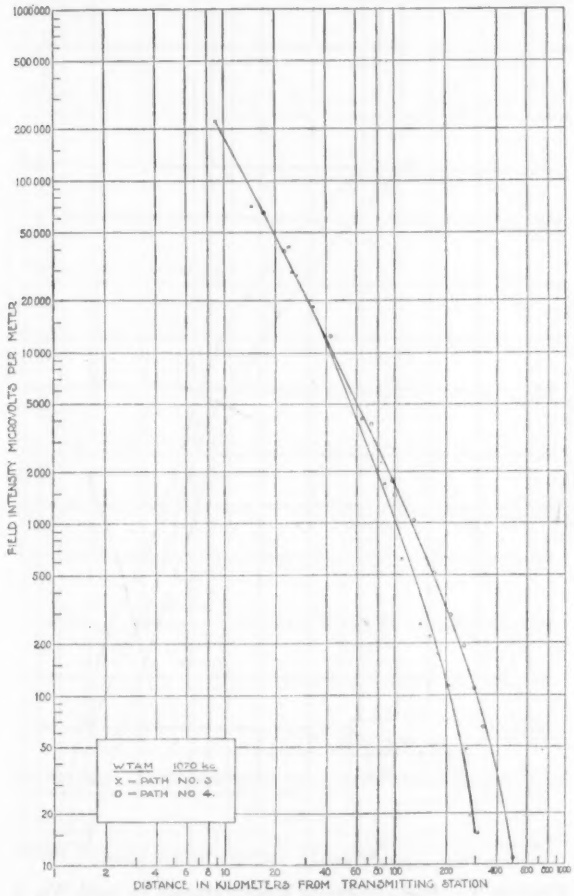

FIGURE 8.—*Field intensities for WTAM on 1,070 kc*

represent the absorption characteristics of this path. Using this value of α in equation (3) the attenuation graphs are determined for 290, 338, 760, and 1,460 kc and are plotted in the dotted graphs of Figures 11 and 12. It may be seen that the experimental points do not fit the graphs, in some cases the points are twenty-four times too far above the graphs, while in other cases the graphs are 3.5 times too far above the points. Similar errors would be indicated if the formula was plotted for the other paths using the average values of α as determined from our measurements. The average value of α used to plot

these graphs might be questioned because the values of α determined from the field intensity varied both with the distance and with the frequency. However, it may be seen from Figures 11 and 12 that such graphs would not fit the experimental data for any value of α chosen; the graphs do not have the proper curvature, thus giving incorrect attenuation factors as the distance is varied, and they do not have enough separation to give proper attenuation factors as the frequency varies. We thus see that for this range of frequencies and for land paths, another formula must be used.

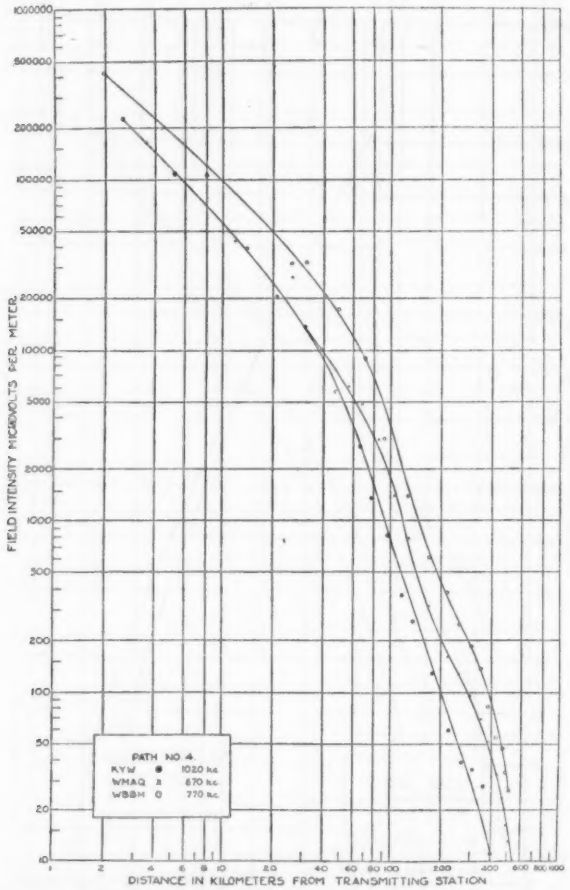

FIGURE 9.—*Field-intensity measurements on path No. 4*

This is offered by the Sommerfeld theory for which graphs have been made by Bruno Rolf.[3] These graphs apply to ground wave transmission only. Sommerfeld obtained the solution by determining the propagation along the plane surface bounding regions (air and earth) of conductivity σ_1 and σ_2, dielectric constant ϵ_1 and ϵ_2, and permeability μ_1 and μ_2. Rolf has graphed the values of A for the case, $\sigma_1 = 0$, $\epsilon_1 = 1$, $\mu_1 = \mu_2 = 1$, while ϵ_2 and σ_2 are variable and represent the earth constants for the particular path involved. Thus we see

[3] Ingeniors Vetenskaps Akademiens Handlingar Nr. 96, 1929; Proc. I. R. E., vol. 18, pp. 391 to 402 March, 1930.

that our problem becomes one of determining the average values of the radio-frequency dielectric constant and conductivity of the ground for the various paths over which measurements were made. The method of determining these was that described by Rolf.

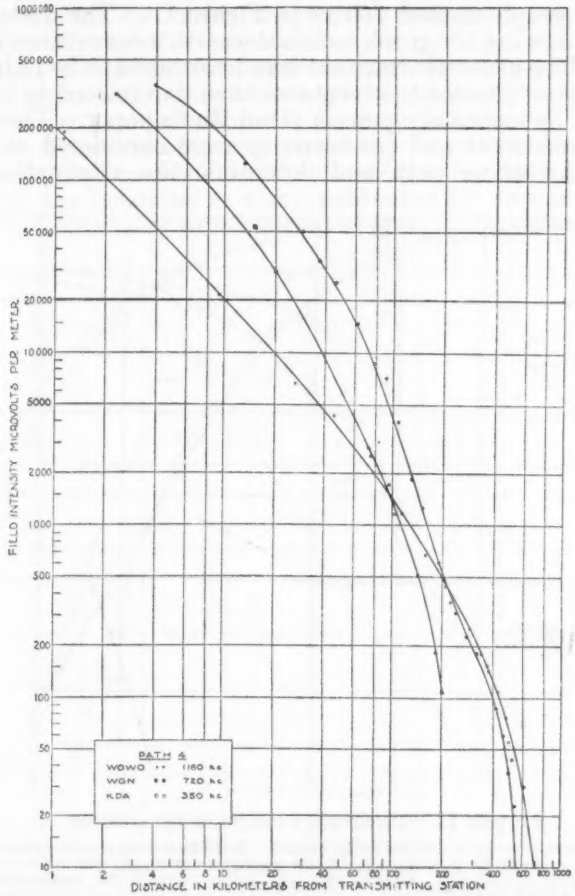

FIGURE 10.—*Field-intensity measurements on path No. 4*

TABLE 2

WJZ=760 kc		WWU=338 kc		WMAL=630 kc		WRC=950 kc		WJSV=1,460 kc		WWV=290 kc	
D	*α*	*D*	*α*	*D*	*α*	*D*	*α*	*D*	*α*	*D*	*α*
km		*km*		*km*		*km*		*km*		*km*	
25	0.00122	73.1	0.000417	11.96	0.000497	4.79	0.00289	3.07	0.000318	37.5	0.000433
40	.00147	97.6	.000419	12.8	.00133	8.1	.00311	8.05	.00275	60.4	.000156
73	.00108	109	.000474	28.5	.00165	10.82	.00163	12.03	.00244	81	.000251
90	.00100	142.6	.000396	48	.00167	12.5	.00174	15.35	.00195	107	.000365
104	.00102	167.6	.000411	72.5	.00116	15.43	.00211	18.1	.00231	132.6	.000335
137	.000895	196.2	.000396	93.5	.00116	20.35	.00208	22.8	.00225	165.2	.000193
170	.000762	214.7	.000425	120	.00102	22.4	.00233	32	.00230	176	.000233
191	.000693	238.3	.000419	145	.000915	26.5	.00237	48	.00169	199	.000159
210	.000704	259	.000462	177	.000741	48	.00186	68.5	.00136	228	.000202
240	.000647	274	.000458	188	.000766	72	.00138	97.5	.00106	247.5	.000254
255	.000647			211.5	.000681	92	.00122	113	.000947	264	.000295
267	.000647			240.5	.000651	118	.00101	138	.000855		
				260	.000577	144	.000901				
				277	.000583	177	.000768				

For path No. 1 the WJZ attenuation factors were plotted and one of Rolf's graphs was fitted to them, thus determining the average conductivity and dielectric constant for path No. 1. Rolf's 10° graph was found to fit satisfactorily after the correction (see equation (4) of Rolf's Proc. I. R. E. paper) for the earth's curvature was made; see solid line graph marked 760 kc in Figure 11. The dotted graph just above shows the 10° graph before the earth's curvature correction was made. The dielectric constant was determined to be 13 by means of Rolf's abac. The conductivity was then determined to be 3.35×10^{-14} e. m. u. by means of equation (1) of Rolf's paper. These values of dielectric constant and conductivity were considered as average values for the whole path and determine the attenuation factor

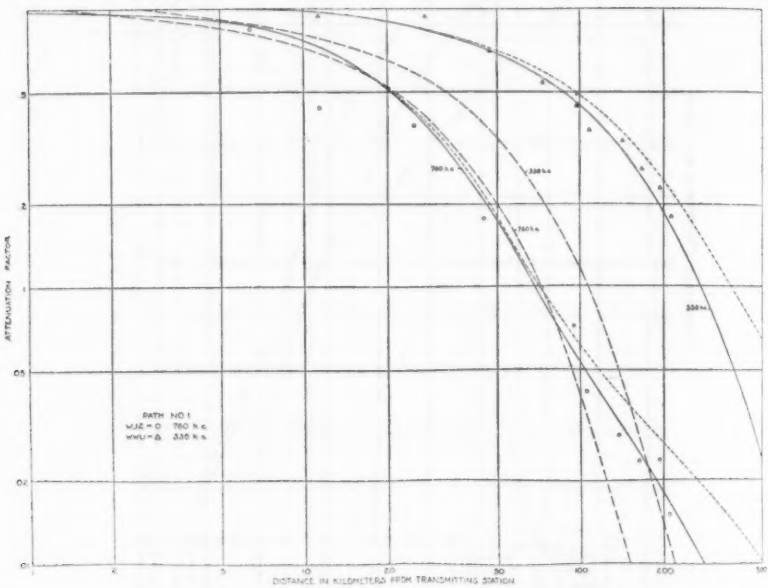

FIGURE 11.—*Attenuation factors versus distance*

Experimental results are shown by the points plotted. Rolf's theoretical graphs corrected for curvature of the earth are shown by the solid lines. Rolf's graphs uncorrected for curvature of the earth are shown by the short dashed lines. Graphs with long dashes represent the Austin-Cohen formula plotted with the average a of Table 2.

graphs for any other frequency over the same path. The theoretical graph for 338 kc is also plotted in Figure 11, the dotted graph just above showing Rolf's graph for that frequency, dielectric constant, and conductivity before correction is made for the curvature of the earth. Theoretical graphs for the other frequencies measured over this path are given in Figure 12 for these same values of dielectric constant and conductivity. It should be noted that when Rolf's theoretical graph for 760 kc was selected the theoretical graphs for the other frequencies over path No. 1 were automatically determined. Over this path the extreme error given by any graph was 48 per cent of the measured value. Usually the discrepancies between the measured values and the graphs were much less than this. Considering the point to point variability of the path, the possibilities of variations of transmitting antenna current, together with the possibility of small

errors in the measurements, it is believed that the agreement between measurement and theory is very good.

For path No. 2 the WRC attenuation factors were used to determine the dielectric constant and conductivity which were found to be $\epsilon=12$, $\sigma=3.22\times10^{-14}$ e. m. u. The theoretical graphs were then drawn in Figure 13 for the three frequencies measured over this path. Attenuation factors of transmissions over path No. 2 from KDKA, 980 kc, were plotted in this figure although the west end of the path was quite mountainous while the eastern end was rolling land. The attenuation factors were found to fit very well the 950 kc graph for this path. Thus the absorption over the mountains was no greater than over the land east of the mountains for corresponding frequencies. In general, the locations at which field-intensity measurements were made in the mountains were selected in open spaces so as to eliminate

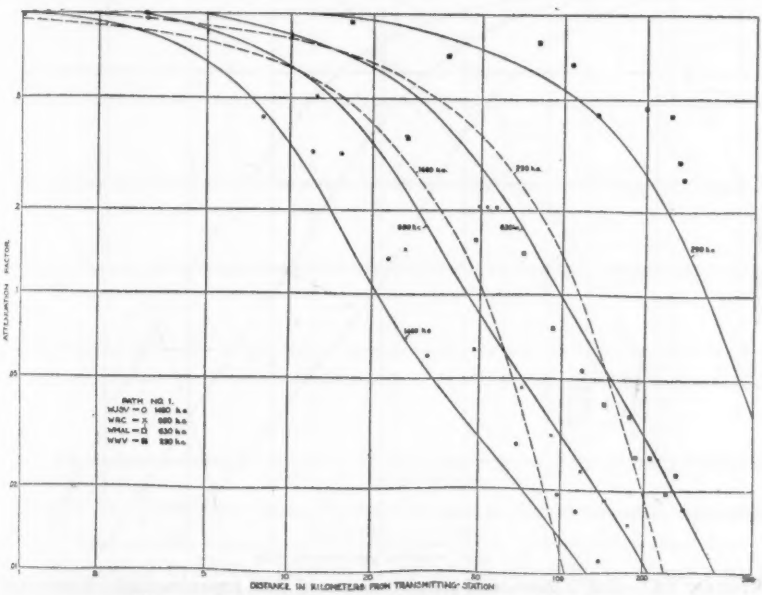
ATTENUATION FACTOR
DISTANCE IN KILOMETERS FROM TRANSMITTING STATION
PATH NO. 1.
WJBV — ○ 1460 k.c.
WRC — × 980 k.c.
WMAL — □ 630 k.c.
WWV — ■ 290 k.c.

FIGURE 12.—*Attenuation factors versus distance*

Experimental results are shown by the points plotted. Rolf's theoretical graphs corrected for the curvature of the earth are shown by the solid lines. The dashed graphs represent the Austin-Cohen-formula plotted with the average a of Table 2.

as far as possible any local shadow effects. However, in two cases this was not done. In a deep valley (Turtle Creek) east of Pittsburgh and about 200 km from Cleveland, WWO's transmission on 344 kc measured less than half the normal value. (Fig. 7.) In this same location WTAM on 1,070 kc measured just about normal. On the east side of and halfway up a mountain at a distance of about 280 km from Cleveland, WWO's transmission measured about 25 per cent below normal while WTAM's transmission was again nearly normal. (Fig. 8.)

For path No. 3 the WTAM attenuation factors were used to determine the dielectric constant and conductivity which were found to be $\epsilon=12$, $\sigma=7.75\times10^{-14}$ e.m.u. This path was not uniform (see fig. 14) as it was mountainous at the east end and fairly flat at the

west end. The transmissions were not absorbed so much over the western part of this path as over the eastern part (probably due to a lower conductivity at the eastern end rather than the mountains, since path No. 2 showed no greater absorption than path No. 1); this caused the more distant WTAM and WWO points to fall below their respective graphs. The measured attenuation factors for KDKA on this path were also plotted. No theoretical graph was drawn, however, since the path from KDKA west was not thought to be similar to that from Cleveland east. It may be noted that the attenuation factors which were obtained in the mountains lie below the 1,070 kc graph while those that were obtained near Cleveland lie above this graph, thus indicating a different type of ground conditions (conductivity) in the mountains than those near Cleveland.

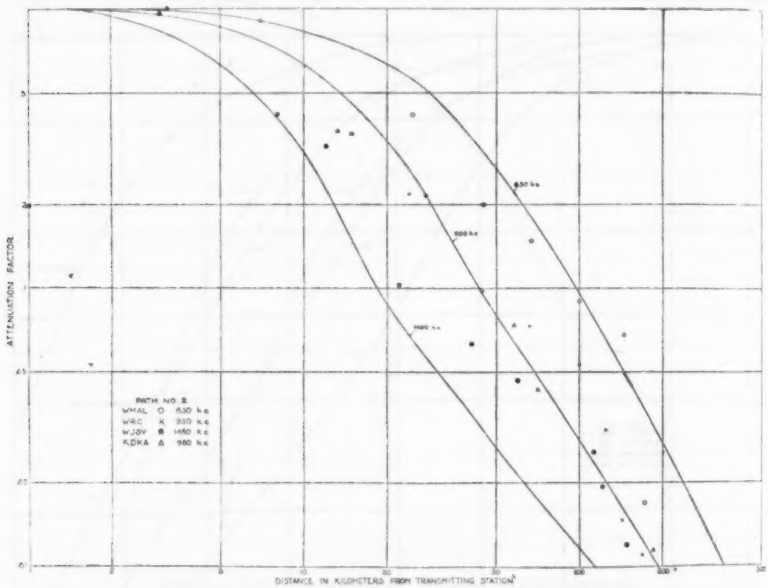

FIGURE 13.—*Rolf's theoretical graphs compared with experimentally determined attenuation factors*

For path No. 4 the WGN attenuation factors were used to determine the dielectric constant and conductivity which were found to be $\epsilon=13$, $\sigma=1.07\times10^{-13}$ e.m.u. It is easily seen in Figures 15 and 16 that the various frequencies measured over this path are not absorbed as much as corresponding frequencies over paths Nos. 1 and 2. The authors believe that this difference is due almost entirely to the difference in the radio-frequency conductivity of the two paths and not so much to the fact that path No. 4 is over more level ground. The fact that the land for paths Nos. 1 and 2 is more wooded [4] than the others might lead to lower values of the conductivity there.

In order to provide a convenient means of estimating the field intensity of the ground wave for any frequency in the broadcast band and for paths east or west of the west side of the Alleghenies,

[4] Barfield, J. I. E. E. (London), vol. 66, p. 204, 1928.

in the latitudes covered by these measurements, graphs are drawn in Figure 17 giving the field intensity versus distance for 300, 600, 1,000, and 1,400 kc. Using the conductivity and dielectric constant as determined for path No. 1, Rolf's graphs were used to determine the proper attenuation factors for the above frequencies east of the Alleghenies (paths Nos. 1 and 2); for the frequencies west of the Alleghenies, the conductivity and dielectric constant as determined for path No. 4 were used. These graphs were drawn for an assumed radiated power of about 11 kw, which corresponds to a field intensity of 10^6 μv/meter at a distance of 1 km from the transmitting station.

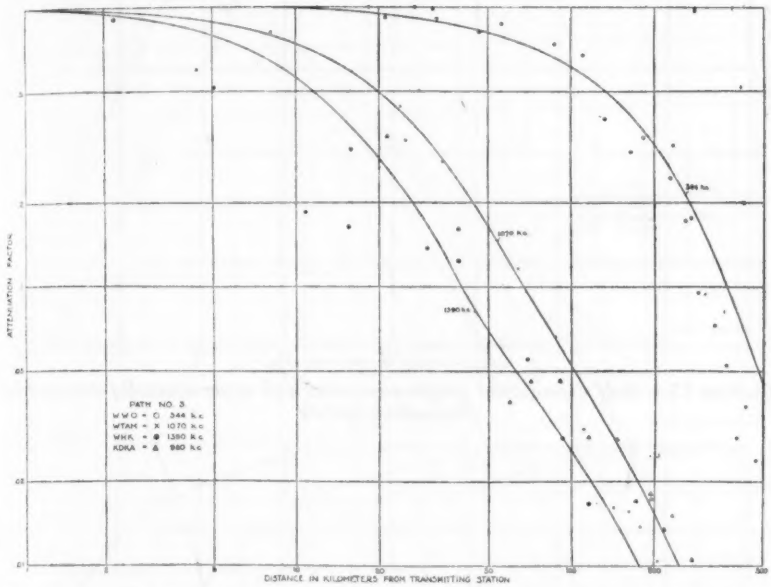

FIGURE 14.—*Rolf's theoretical graphs compared with experimentally determined attenuation factors*

For any other radiated power P_r given in kilowatts, the given field intensities must be multiplied by a factor

$$K = 0.3\sqrt{P_r} \tag{4}$$

It should be noted at this point that the radiated power is always somewhat lower than the power input to the antenna and for frequencies in the broadcast band the radiated power is usually less than half the rated power. If field-intensity measurements have been made near the transmitting station the radiated power may be approximately determined by means of the formula[5]

$$\text{Radiated power} = P_r = (F\,D/3A)^2\ 10^{-10} \text{ kilowatts} \tag{5}$$

where

F = field intensity in microvolts per meter.
D = distance from transmitting station in kilometers.
A = attenuation factor.

The attenuation factor to be used may be determined for any given path, frequency, and distance from Figures 11 to 16, inclusive. Thus in order to determine the daytime (ground wave) field intensity

[5] Pierce, Electrical Oscillations and Electric Waves, ch. 9.

in any direction and at any distance from the transmitter for broadcasting stations east of Chicago it is merely necessary to make a

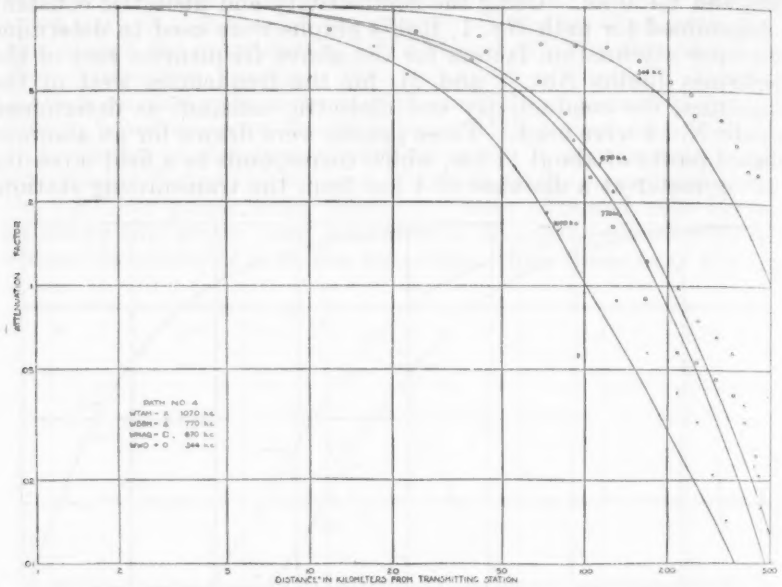
ATTENUATION FACTOR
DISTANCE IN KILOMETERS FROM TRANSMITTING STATION
PATH NO. 4
WTAM = A 1070 kc
WGBM = B 770 kc
WMAQ = C 670 kc
WWO = D 344 kc

FIGURE 15.—*Rolf's theoretical graphs compared with experimentally determined attenuation factors*

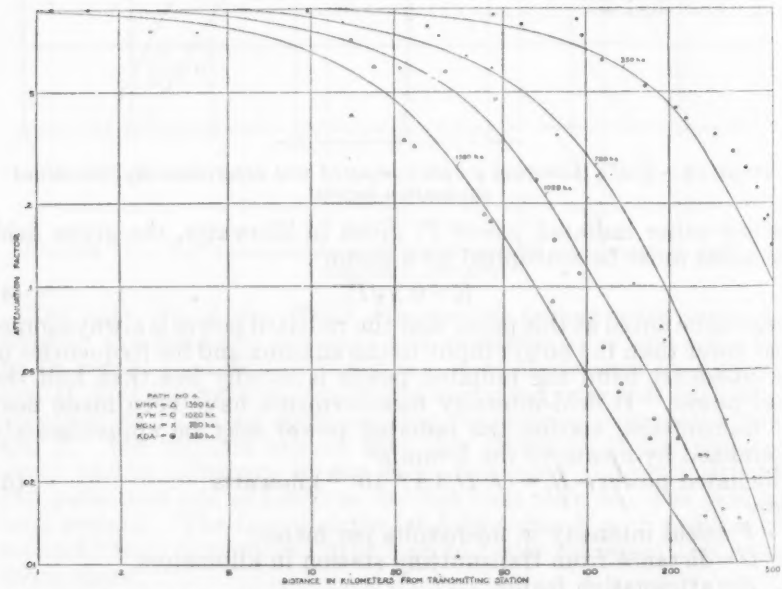
ATTENUATION FACTOR
DISTANCE IN KILOMETERS FROM TRANSMITTING STATION
PATH NO. 4
WMC = A 1390 kc
KYW = C 1020 kc
WGN = X 720 kc
KDA = B 500 kc

FIGURE 16.—*Rolf's theoretical graphs compared with experimentally determined attenuation factors*

single measurement of the field intensity in the direction from the transmitting station in which other values are to be estimated. This, together with the value of A as determined from the graphs assuming

the constancy of the ground conductivity with time,[6] may be substituted in equation (5) to give the power radiated in that direction. The factor K may then be determined from equation (4); this factor

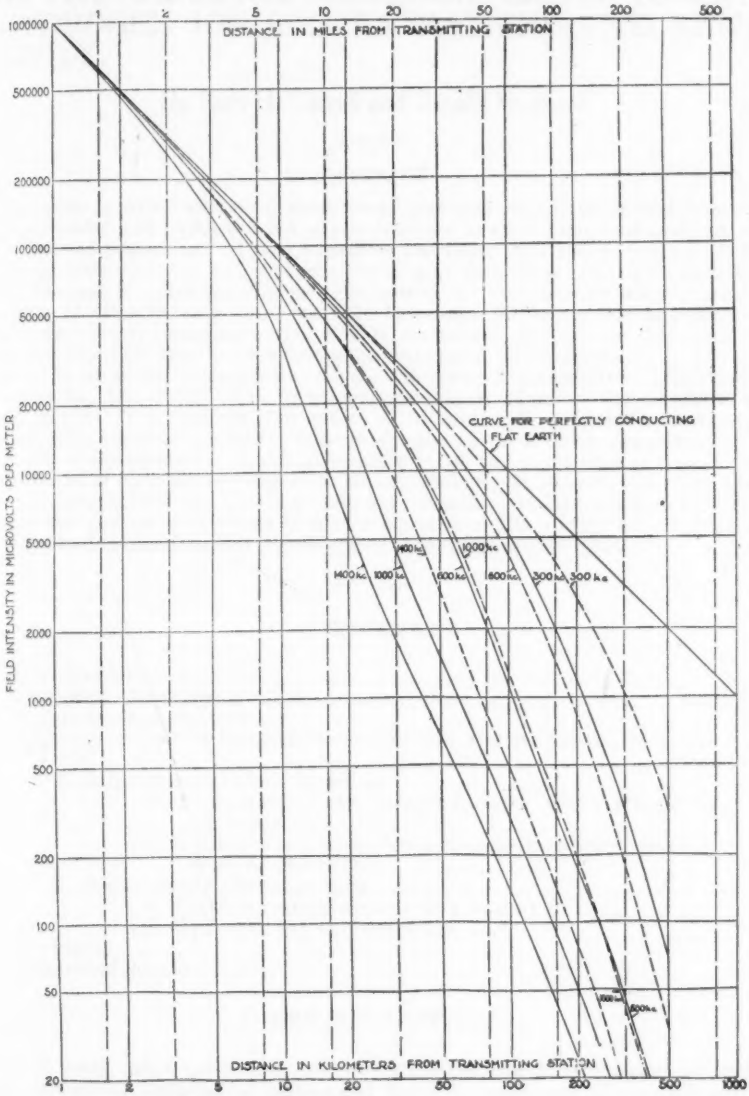

FIGURE 17.—*Field intensity versus distance*

Solid graphs predict the field intensity of the ground wave for $\epsilon = 12$ $\sigma = 3.22 \times 10^{-14}$ e.m.u. paths Nos. 1 and 2. Dashed graphs predict the field intensity of the ground wave for $\epsilon = 13$ $\sigma = 1.07 \times 10^{-13}$ path 4. Radiated power assumed as 11 kw.

when multiplied by the field intensities in Figure 17 gives the required field intensity.

WASHINGTON, January 19, 1932.

[6] Continuous automatic field intensity records of transmissions from WJZ (760 kc), Bound Brook, N. J. over a path 275 km long show total variations of daytime field intensities of about 30 per cent over a period of a year.

THE PHOTOGRAPHIC EMULSION: SILVER ION AND HYDROGEN ION CONCENTRATIONS AND SENSITIVITY

By Burt H. Carroll and Donald Hubbard

ABSTRACT

The paper is introduced by discussions of previous experimental and theoretical work on silver and hydrogen ion concentrations in emulsions, and description of experimental technique. These variables are taken up first according to their effects on afterripening, and second according to their direct effects on sensitivity when changes in afterripening are eliminated (in experiments after digestion). The rate of afterripening increases with increasing silver ion concentration and increasing pH; the corresponding effects on sensitivity are much larger than those produced by the direct effect of environment (after digestion). The combination of silver ion with gelatin reduces the effect of excess silver. Illustrations are given for the distribution of excess bromide or silver in the emulsion with changing pH. The desensitizing action of bromide (after digestion) is found to increase with increasing acidity; conversely, the effect of pH is dependent on the silver ion concentration. Spectral sensitivity of the emulsions is found to be independent of hydrogen or silver ion concentrations; these variables must, therefore, influence sensitivity through secondary reactions in latent image formation. Results are discussed in terms of a new concept of the adsorption of gelatin to silver bromide, based on the "zwitterion" theory of ampholytes.

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I. INTRODUCTION

It has long been common knowledge that the photochemical sensitivity of silver halides is increased by the presence of soluble silver salts. The effect of acidity or alkalinity has been less clearly recognized, but early work on both these variables in silver bromide-gelatin emulsions is to be found in Eder's Handbuch.[1] While these variables must always be studied by using acids or alkalies in one case, and soluble silver salts or bromides in the other, it is now recognized that the results of experiments upon the effects of acids and bases may most frequently be generalized by considering the resulting concentration

[1] J. M. Eder, Ausführliches Handbuch der Photographie, vol. 3, 5th ed., pp. 50, 131, 1903.

(or activity) of the hydrogen ion which is the common variable in all such experiments. In silver bromide emulsions, the effects of adding silver salts or bromides may similarly be expressed in terms of the resulting silver ion concentrations. In aqueous solutions the concentrations of hydrogen and hydroxyl ions may always be expressed by the relation $[H^+]\times[OH^-]=10^{-14}$. Similarly, in silver bromide emulsions, at 30° C., $[Ag^+]\times[Br^-]=9.2\times10^{-13}$. The solubility product of silver bromide here plays a part analogous to the dissociation product of water, since the enormous available surface of the highly disperse silver bromide insures that the emulsion may at all times be considered saturated with respect to this salt. The silver ion concentration may be determined by the potential of the silver-silver bromide electrode exactly as the hydrogen ion concentration is determined by the hydrogen electrode. It is also possible to express the results in terms of the excess of one material or another which is present, but as gelatin combines both with hydrogen ions and silver ions,[2] the relations of the chemical composition to the ion concentrations may be quite complicated. Data on these relations of chemical composition to ion concentrations will be given in this paper, but we will in general discuss the results in terms of the ion concentrations. As just explained, silver ion and bromide ion concentrations are interrelated like hydrogen ion and hydroxyl ion concentrations and either may be used to specify a given condition. The silver ion-gelatin combination being dependent on the hydrogen ion concentration, the silver ion and hydrogen ion concentrations of an emulsion are not entirely independent variables and are, therefore, treated together in this paper.

The relation of any variable to sensitivity of photographic emulsions changes with the stage of emulsion making which is under consideration. We shall deal in this paper only with the effects on the washed emulsion, omitting the ripening process before washing. Even with this limitation of scope it seems necessary to distinguish between two possible mechanisms. In the first place, both silver and hydrogen ion concentrations of an emulsion during digestion will influence sensitivity through the rate of afterripening; we[3] have previously given considerable data on the effect of silver ion concentration on afterripening, and preliminary results on hydrogen ion concentration. In the second place, there may be an effect caused directly by the existence of a given hydrogen or silver ion concentration in the emulsion at the time of exposure. Sheppard and Wightman[4] have referred to this as the effect of environment on sensitivity; they do not specifically define the term, but we infer that it means the thermodynamic environment of the silver halide grains, and we shall use it in that sense. The effect of environment might a priori be expected to be reversible; that is, on reproducing a given set of conditions, the corresponding sensitivity should also be reproduced. The afterripening process is, in contrast, irreversible, but obviously both effects must be superimposed when the hydrogen ion concentration of an emulsion is changed before afterripening.

This paper presents data on afterripening under a wide range of both hydrogen and silver ion concentrations, and on the relation of sensi-

[2] Carroll and Hubbard, B. S. Jour. Research, vol. 7 (RP376), p. 811, 1931.
[3] Carroll and Hubbard, B. S. Jour. Research, vol. 7 (RP340), p. 219, 1931.
[4] Sheppard and Wightman, Phot. J., vol. 69, p. 22, 1929.

tivity to these variables under conditions such that the afterripening effect has been eliminated. Similar experiments with emulsions containing sensitizing dyes will be reported in a separate communication.

II. REVIEW OF LITERATURE

We are indebted to Rawling and his associates [5] at the British Photographic Research Association for the first quantitative studies of the effect of the hydrogen ion concentration of emulsions on their sensitivity. In many of their experiments the pH of portions of the emulsion was adjusted to the desired value (by addition of acid or alkali) during or after washing, and the total effect measured after the separate portions were digested "to equilibrium." In another series they changed the pH of emulsions two or more times during digestion, coating test plates after each change, and found that the sensitivity changed immediately with the change of the hydrogen ion concentration and returned to its original value (corrected for the slow continuous increase due to afterripening) when the original pH was restored. Rawling refers to this latter as the "reversible effect," as distinguished from the slow "irreversible effect" of afterripening. The ratio of speed at two values of pH was found to be independent of emulsion formula, of grain size within the emulsion, or of the presence of nuclei derived from sulphur sensitizers, but was dependent on the gelatin. Fog and the shape of the characteristic curve were also reported to be independent of the pH during afterripening, and no extension of spectral sensitivity to longer wave lengths was detected.

While the emulsions in the earlier papers are described as "digested to equilibrium," the curves in the 1929 paper indicate that at the higher pH the afterripening was still progressing slowly during the experiments. At pH 5 the afterripening stopped entirely, and there was even a slight decrease in sensitivity in some cases.

Sheppard and Wightman [6] confirmed Rawling's observation of a reversible change in sensitivity when the pH of liquid emulsions was changed before coating. They found that some irreversible process occurs on drying, since the sensitivity of dried plates was not affected by immersing them in buffer solutions ranging from pH 3 to 11. Their data in some cases show a distinct increase in fog with pH.

There has been little quantitative work dealing with the effect of silver ion concentration on sensitivity. Sheppard and Wightman [7] demonstrated that sensitivity is appreciably reduced by the presence of 0.001 *N* soluble bromide, the effect increasing with concentration. Control experiments proved that the results could not be explained by action of the bromide on the latent image or by absorption of light by its solution. In dilute solutions at least, sensitivity was restored by washing out the bromide before exposure. When plates were exposed under 0.01 *N* silver-nitrate solution, acidified to pH 4, and the silver removed before development (by washing with dilute acid), there was no effect on sensitivity.

Fajans and his students [8] have investigated the effect of adsorbed ions on the sensitivity of silver bromide. As their experiments dealt

[5] Rawling and Glassett, Phot. J., vol. 66, p. 495, 1926. Rawling and Vick, Phot. J., vol. 67, p. 42, 1927. Rawling, Phot. J., vol 69, p. 83, 1929. Rawling, Proc. 7th Internat. Cong. Photography (London), p. 192, 1928.

[6] See footnote 4, p. 482.

[7] Sheppard and Wightman, Phot. J., vol. 69, p. 134, 1929.

[8] Summary in Lüppo-Cramer, Grundlagen der Phot. Negativverfahren, p. 633.

with the photolysis of colloid-free material, extension of their results to developable sensitivity in emulsions must be justified by experiment. They found that silver bromide with adsorbed bromide ions had the same spectral sensitivity as pure material, the threshhold being at about 430 mμ. Adsorbed silver or hydroxyl ions extended the spectral sensitivity to at least 615 mμ; careful measurements detected a corresponding change in spectral absorption, although the increase in rate of photolysis was much greater than the increase in absorbed energy under the same conditions. Fajans attributes the effects of the adsorbed ions to deformation of the outer electron shells of the surface bromide ions in the silver bromide by electrostatic attraction, which facilitates the transfer of electrons from bromide to silver ions. Luppo-Cramer [9] tested for the existence of this effect in silver bromide-gelatin emulsions by bathing them in dilute NH_4OH or NaOH solutions, washing, and drying. Plates thus treated were blackened by light without development much more rapidly than before treatment; their sensitivity to red light with development was also increased, but the sensitivity to white light with development was little affected. Factors other than adsorbed hydroxyl ions may have entered into these results.

Various hypotheses have been offered to explain the effect of hydrogen ion concentration on sensitivity, especially the reversible effect.

Slater Price [10] has described experiments by Rawling and Owens which show that the rate of reaction of gelatin with hypochlorite or hypobromite increases with increasing pH. The equilibrium in the solutions shifts with increasing pH toward the OCl^- or OBr^- ions, which are apparently the reactive forms. This indicates that the pH effect on sensitivity may be explained by change in the rate of reaction between the gelatin and the bromine liberated on exposure. A serious difficulty is introduced by the quantitative agreement between the reactivity of three samples of gelatin, although the photographic effect of pH is rarely the same for two different samples of gelatin. However, the conditions chosen for study of the reaction appear to have been unsuitable for the detection of such differences. In the illustrative data the weight of available chlorine in the hypochlorite solution was slightly greater than the weight of gelatin, corresponding to a very large chemical excess; in the curve of Figure 1, the gelatin had absorbed up to 6 per cent of its weight of chlorine. In view of the very small quantity of bromine liberated in the formation of the latent image, it seems as though differences between samples of gelatin might be more obvious in experiments where the gelatin was in great excess and only the earliest stages of the reaction were studied.

Gramse [11] has also used the hypothesis of reaction between the gelatin and bromine liberated by photolysis as a factor in the formation of the latent image. He demonstrated experimentally that the rate of reaction between bromine and gelatin increases with increasing pH, explaining this by the formation of hydrobromic acid, which retards the reaction unless taken up by alkali. He also offers the suggestion that since iodine or sulphur can act as halogen carriers in this reaction, the effect of silver iodide or sulphide on sensitivity may be explained in terms of this function.

[9] Lüppo-Cramer, Phot. Ind., vol. 22, p. 357, 1924.
[10] Slater Price, Phot. J., vol. 71, p. 59, 1931.
[11] Gramse, Zeit. f. wiss. Phot., vol. 30, p. 40, 1931.

Calzavara [12] has recently suggested that the effect of pH on sensitivity may be explained in terms of its effect on oxidation-reduction potential, but has apparently not given any experimental evidence in support.

In a speculative paper [13] Sheppard has suggested that adsorption of gelatin to silver halides takes place at azine linkages which are in equilibrium with heterocyclic ring structures not capable of similar oriented adsorption. As the equilibrium between the dif-

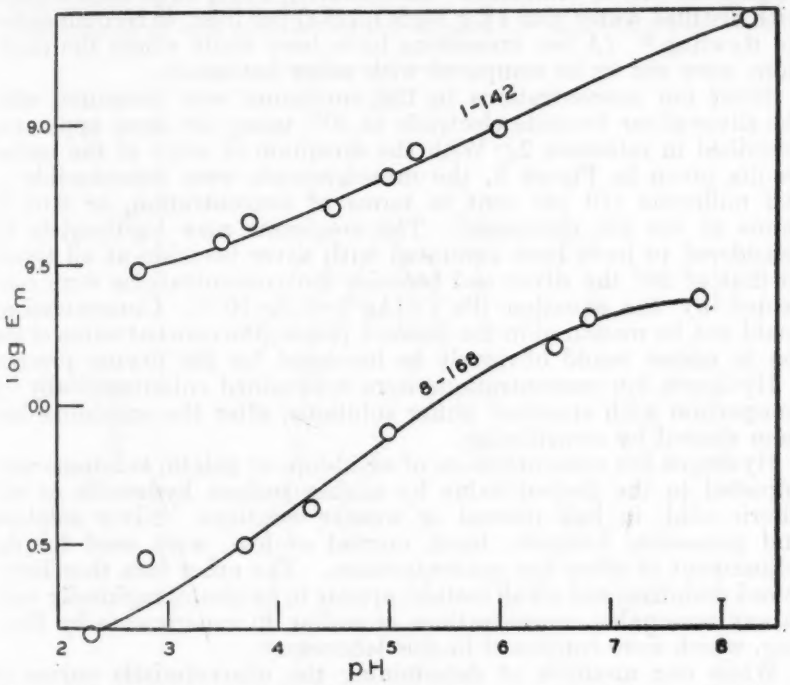

FIGURE 1.—*Variation in sensitivity of emulsions with pH during digestion for constant time*

ferent conditions of the nitrogen would be dependent on the hydrogen ion concentration, this might affect sensitivity through changes in the protective action of the gelatin.

III. EXPERIMENTAL TECHNIQUE

The methods of emulsion making and sensitometry in use in the photographic emulsion laboratory of the Bureau of Standards have recently [14] been described in detail in connection with our communication on afterripening. We shall here use the same letters to designate the type emulsion formulas given in detail in that paper.

[12] Calzavara, Sci. et Ind. Phot. (2), vol. 2, p. 472, 1931.
[13] Sheppard, Phot. J., vol. 69, p. 330, 1929.
[14] See footnote 3, p. 482.

There has been one change in the methods of emulsion making. During the period of most of the experiments on afterripening, the Potomac River, which is the source of the Washington water supply, was very low and clear as the result of drought, being fed largely by springs in limestone formations. The quality of the water was, therefore, quite constant. Since January, 1931, surface water has made up a much larger proportion of the flow and the quality is less reliable; tests indicate the presence of traces of sensitizing and fogging materials. Emulsions since March, 1931, have been washed with distilled water plus 1¼ g $MgSO_4.7H_2O$ per liter, as recommended by Rawling.[15] (A few exceptions have been made where the emulsions were not to be compared with other batches.)

Silver ion concentrations in the emulsions were measured with the silver-silver bromide electrode at 30°, using the same apparatus described in reference 2. With the exception of some of the earlier results given in Figure 3, the measurements were reproducible to ±2 millivolts (10 per cent in terms of concentration, or 0.03 in terms of the ion exponent). The emulsions may legitimately be considered to have been saturated with silver bromide at all times, so that at 30° the silver and bromide ion concentrations were connected by the equation $[Br^-]\times[Ag^+]=9.2\times10^{-13}$. Concentrations could not be measured in the finished plates; the concentration of the ion in excess would obviously be increased by the drying process.

Hydrogen ion concentrations were determined colorimetrically by comparison with standard buffer solutions, after the emulsions had been cleared by centrifuging.

Hydrogen ion concentrations of emulsions or gelatin solutions were adjusted to the desired value by adding sodium hydroxide or sulphuric acid, in half normal or weaker solutions. Silver sulphate and potassium bromide, tenth normal or less, were used for the adjustment of silver ion concentrations. The other ions thus introduced (sulphate and alkali metals) appear to be photographically inert in any reasonable concentrations according to experiments by Rawling, which were confirmed in this laboratory.

While our methods of determining the characteristic curves of experimental emulsions were unchanged, the expression of the sensitivity in numerical terms has been altered in some cases. We have continued to use the speed number derived from inertia where a series of emulsions had satisfactory straight lines in their characteristic curves, and could be compared at the same γ. In following changes such as those occurring during afterripening, where both speed and contrast increase, it was found more satisfactory to use the speed number derived from minimum useful gradient, which appears to express the change in effective sensitivity better than any other single number. A minimum gradient of 0.2 for 6-minute development was normally used, but on some of the steeper curves a higher value could be read more accurately and appeared better to represent the results judged from the entire curve.

[15] See footnote 5, p. 483.

IV. HYDROGEN ION-SILVER ION-GELATIN EQUILIBRIUM AND ITS EFFECTS ON SENSITIVITY

1. ADJUSTMENTS BEFORE DIGESTION

(a) HYDROGEN ION CONCENTRATION, WITH VARYING TIME OF DIGESTION

When the pH of an emulsion is adjusted before digestion, and the sensitivity determined after constant time and temperature of digestion, both the reversible effect on sensitivity and the effect on rate of afterripening are involved in the final result. We have given a few illustrations of this case in Tables 17 and 18 of reference 3. Similar

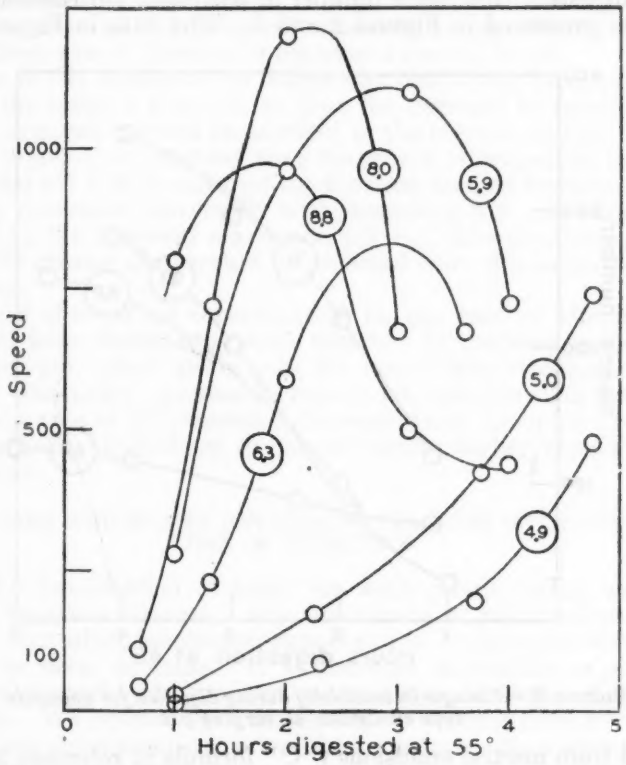

FIGURE 2.—*Changes in sensitivity during digestion for neutral type emulsions at varying pH*

data covering a wider range of pH are given in Figure 1 of this paper; the different portions of the emulsions were adjusted in pH, then all digested for two hours at 45°. Both emulsions were of the ammonia type. Bromide ion concentrations in 8–168 varied with pH from 3 to 12×10^{-5}; in 1–142 they were not determined, but were probably about one-fifth these amounts. In these emulsions there was a distinct minimum of contrast around the isoelectric point. The variation in sensitivity was most conveniently represented by the exposure required for a given minimum gradient. In this case it was necessary to use a gradient of 0.5 on the curve for 12 minutes development, which was least affected by the pH. Plotting the

logarithm of this exposure against pH, the curves are approximately linear in both cases; that is, the change in sensitivity was roughly constant for unit change of hydrogen in concentration. The slope of the curve for 8–168 is larger, which may be ascribed to its greater bromide ion concentration; as previously explained in reference 3, page 240, this increased slope is to be expected because higher bromide ion concentrations are less affected by pH so that the true pH effect is less opposed by increasing $[Ag^+]$.

The results of comparison on a constant time of digestion were given because this condition might be encountered in practice. More complete information was obtained from curves of sensitivity against digestion time for a number of hydrogen ion concentrations. These are presented in Figures 2 and 3. The data in Figure 2 were

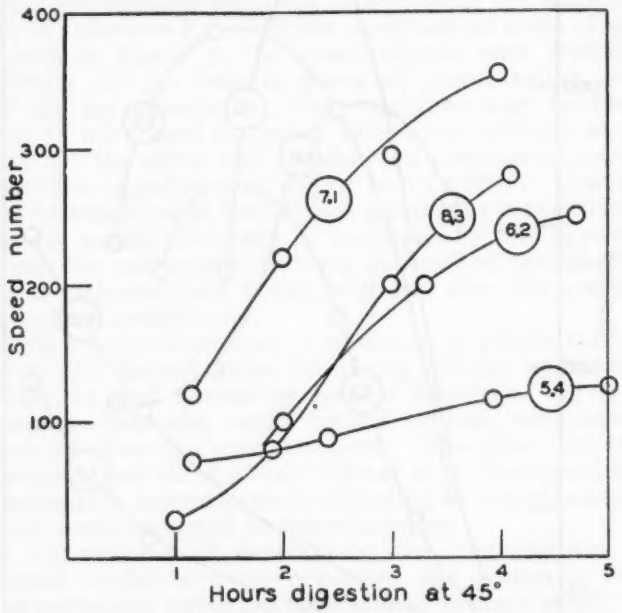

FIGURE 3.—*Changes in sensitivity during digestion for ammonia type emulsions at varying pH*

obtained from neutral emulsions ("C" formula in reference 3, p. 227, using 4 per cent AgI, 25 per cent excess NH_4Br and 25-minute mixing time at 65°). These were all made from the same batch of washed gelatin, and washed with distilled water; the pH of the emulsions was 4.9 as washed, and was adjusted before digestion by addition of NaOH. Bromide ion concentrations were all within the range 6.5 to 13×10^{-4} *N*. Sensitivity is represented by the speed calculated as the reciprocal of exposure for minimum useful gradient, in this case the standard value of 0.2 gradient for 6-minute development. The data in Figure 3 were obtained from ammonia process emulsions ("A" formula in reference 3, p. 226, with 5 per cent AgI); these were made from untreated gelatin and washed with distilled water. The pH as washed was 8.3; it was adjusted before digestion by addition of H_2SO_4. Bromide ion concentrations were within the range 6.5 to 9.0×10^{-4} *N*.

It was found unusually difficult to reproduce results in these experiments. However, it is evident that the rate of afterripening increased rapidly with increasing pH between 5 and 7. The increase in rate is greater than the increase in maximum sensitivity, so that it is not merely the result of the reversible pH effect which would increase sensitivity at all stages of ripening.

In both series of emulsions there was a decrease in maximum sensitivity for pH>8, with no indication of a decrease in rate of afterripening. In the neutral emulsions, there was serious fog at pH 8 or higher; one batch digested at 9.7 was completely ruined. The NaOH used for adjustment of pH was tested for the presence of fogging impurities by neutralizing a portion of it larger than used for adjustment and adding this to a portion of emulsion during afterripening at pH 7.3; there was no increase in fog over a control batch.

The fog in the ammonia emulsions was practically independent of pH over the range 5.4 to 8.3, so that the decrease in sensitivity at pH>8 in this case can not be ascribed to the increase in fog. On the available evidence we may say that the rate of afterripening increases rapidly from pH 5 to 7, and that the time required to reach maximum sensitivity decreases continually with increasing pH. At alkalinities greater than the practical maximum, pH 8.5, deterioration is rapid, and may be greater than would be expected from the increased tendency to fog.

The effect of silver ion concentration on the rate of afterripening has already been described in some detail.[16] In contrast to the effect of hydrogen ion, which alters both the rate of afterripening and the maximum sensitivity, increased bromide ion concentration may only decrease the rate of afterripening, the sensitivity for optimum digestion being little affected up to concentrations higher than those in common use.

(b) HYDROGEN AND SILVER ION CONCENTRATIONS WITH CONSTANT TIME OF DIGESTION

Since the combination of silver ion with gelatin varies with the hydrogen ion concentration,[17] any adjustment of pH involves also a change of free silver ion concentration and in bromide or silver ions adsorbed to silver bromide. It is therefore impossible to give the effects of silver and hydrogen ions on sensitivity distinct and separate treatments. We present first the results of varying both silver and hydrogen ion concentrations in emulsions before afterripening them by digestion.

All four emulsions were made by the following formula:

Bromide solution	Water	ml	175
	KBr (12.5 per cent excess)	g	23.7
	Gelatin	do	10.0
Silver solution	Water	ml	225
	$AgNO_3$	g	30.0

The silver solution was added to the bromide solution in 6 to 7 minutes at 65.0° ± 0.2°. Centrifugal washing,[18] in three batches, was started at 9 to 10 minutes from the start of mixing and finished at 36 to 38 minutes. The silver bromide was resuspended in 400 ml of

[16] See footnote 3, p. 482.
[17] See footnote 2, p. 482.
[18] Carroll and Hubbard, J. Phys. Chem. vol. 31, p. 910, 1927.

1 per cent gelatin, at a pH of 4.7 − 4.9. Two batches of this size were then combined, and the silver ion concentration adjusted by appropriate additions of silver sulphate solution; the suspension was then divided into eight 100 ml portions, and left in the refrigerator over night. The next day the separate portions were carefully remelted as needed, centrifuged again, and the final emulsion made by suspension of the silver bromide in 12.5 g gelatin and 235 ml water. The pH of the eight batches of emulsion was adjusted by additions of sulphuric acid and each was digested for two hours at 45°. In order to reduce fog in the batches with higher silver ion concentrations, gelatin which had been treated with ammonia and thoroughly washed was used for emulsifying the silver bromide after centrifuging. Pure bromide emulsions made with this partly deactivated material

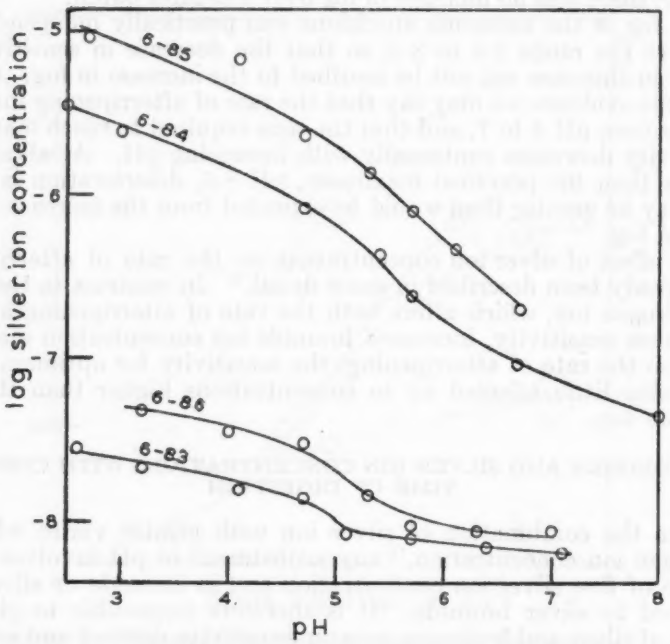

FIGURE 4.—*Variation of silver ion concentration of emulsions with pH*

necessarily had relatively low sensitivity. Sensitometric tests were made with a special *p*-aminophenol developer [19] found to give speed numbers equivalent to the usual pyrogallol formula on the normal batches of these emulsions, and less fog on those with increased silver ion concentration.

Figure 4 gives the relation between silver and hydrogen ion concentrations in these emulsions. Silver ion concentrations in the first resuspensions, which determine the range of silver ion concentrations in the final emulsions, were as follows:

[19] Formula:

p-aminophenol hydrochloride	g	3.6
Na_2SO_3	do	25.0
Na_2CO_3	do	25.0
KBr	do	0.6
Water to make	liter	1.0

2, 4, and 8 minutes brush development at 20° C.

TABLE 1

	N
6–85	6.6×10^{-4}
6–84	8.2×10^{-5}
6–86	6.1×10^{-9}
6–83	8.8×10^{-10}

It is evident that the slope of the curves is greater at higher silver ion concentrations. This is readily predicted from the data in reference 2 on the combination of silver ion and gelatin; silver combined with unit weight of gelatin becomes increasingly dependent on pH at

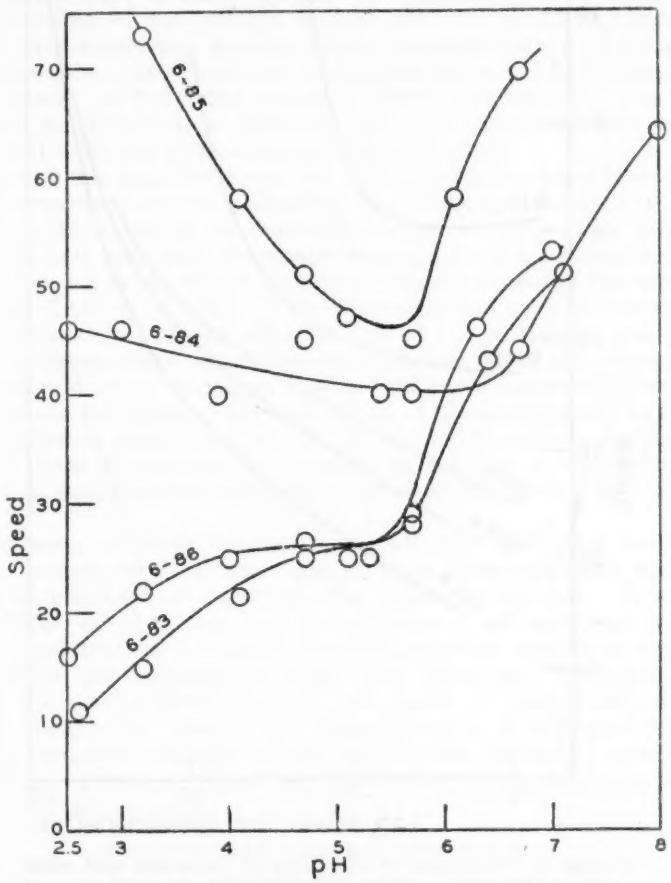

FIGURE 5.—*Variation of sensitivity of emulsions with pH during digestion, for constant time of digestion*

higher silver ion concentrations. The concentration of free silver ions is therefore more affected under these conditions by the change in combined silver with varying pH. It will further be noted that although the curves show an appreciable break at the isoelectric point of gelatin, they are essentially continuous.

In Figure 5, speeds of these same emulsions are plotted against pH. For these emulsions, speed is expressed as the reciprocal of the expos-

ure necessary for a gradient of 0.3 at the maximum development time; while there were satisfactory straight line portions of the characteristic curves, γ changed with pH, so that the speed from inertia alone was not the best single number expressing sensitivity. Within the normal range of pH (5.5 or higher) the sensitivity for constant digestion time in each curve shows the usual rapid increase with increasing pH. Comparing the four curves, it increases with increas-

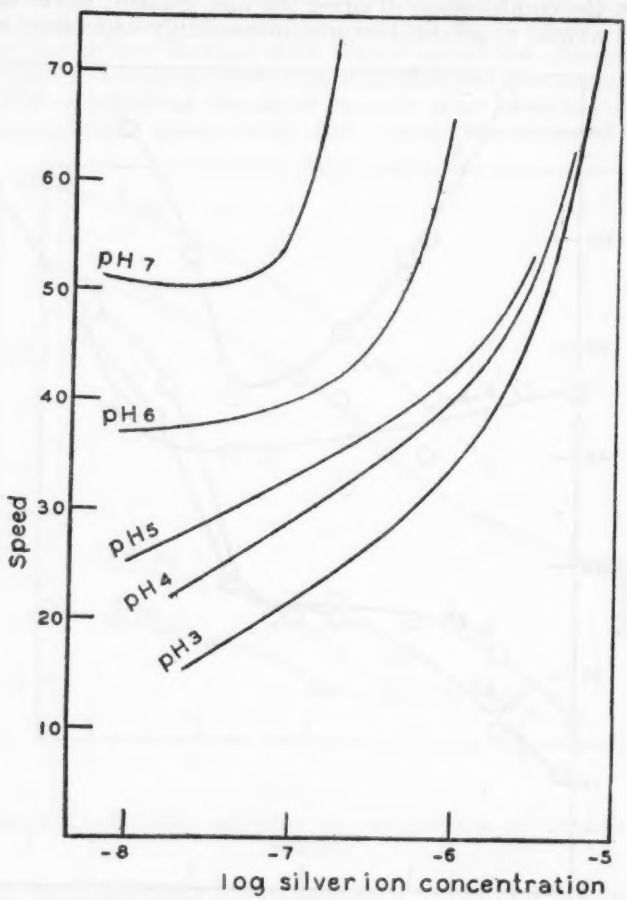

FIGURE 6.—*Variation of sensitivity of emulsions with silver ion concentration during digestion, for constant time of digestion*

ing silver ion concentration, as is to be expected from the effect of silver ion concentration on after ripening.[20] (The last two points of the curve for 6–84 are out of place in both Figures 4 and 5, and possibly unreliable.) All four curves have points of inflex ion or minima at pH 5 to 5.5; the corresponding characteristic curves have minimum values of γ in this region. On the acid side of the isoelectric point the shape of the curves is highly dependent on the silver ion

[20] See footnote 3, p. 482.

concentration. We have already noted [21] that on changing the hydrogen ion concentration of an emulsion, the resulting change in silver ion concentration is in the direction which tends to counteract the photographic effect of the original change of pH. Under ordinary conditions, as in emulsion 6–83, the change in silver ion concentration is relatively small and the rate of afterripening increases with pH, although the shape of the curve is decidedly different on the two sides of the isoelectric point. In the emulsions with excess silver (6–84 and 6–85) the silver ion concentration increases so rapidly with decreasing pH that its effect on the rate of afterripening more than offsets the effect of the acidity, and at pH <4.7 sensitivity actually increases with increasing acidity, under constant time and temperature of digestion. It should be emphasized that in all batches of a given emulsion, as 6–85, the excess of silver over bromine was constant, but its distribution between free and combined ions varied with the pH with the consequences here indicated.

In Figure 6 the data from the two previous figures have been combined as smoothed curves indicating the change in sensitivity with silver ion concentration at constant values of pH. The original expectation had been that these curves would show a sudden increase in sensitivity when the silver ion concentration exceeded the equivalence point ($[Ag^+]=10^{-6}$ N). This is roughly the case for emulsions at pH 5 or less, but on the alkaline side of the isoelectric point the point of increase comes at decreasing values of silver ion concentration. It should be remembered that actual equivalence of silver and bromine in the emulsion at normal values of pH corresponds to silver ion concentration much less than 10^{-6} N. At pH 7, and concentrations similar to these emulsions, the bromide in solution is equivalent to the silver in combination with the gelatin at $[Ag^+]=2\times10^{-8}$ ($[Br_-]=5\times10^{-5}$).

In discussion of these emulsions, no attempt has been made to calculate changes in silver ion concentration from changing acidity, since the emulsions were digested after adjusting the pH. It is further doubtful whether the data in reference 2 are accurate for all samples of gelatin; the available emulsion gelatins appear to vary in their capacity for combination both with silver and hydrogen ions although the qualitative behavior and order of magnitude of the effects is always the same. The measurements of reference 2 were made on de-ashed gelatin which fulfills the tentative specifications [22] of the American Chemical Society for a standard gelatin as to source and ash content.

2. ADJUSTMENT AFTER DIGESTION

(a) SILVER ION CONCENTRATION AT CONSTANT pH

Data in this section were obtained from emulsions which had been digested nearly to maximum sensitivity before adjustment of the silver ion concentration; while we do not feel justified in referring to them as at equilibrium, the rate of change of sensitivity with time was nearly at its lowest point. The emulsions were usually digested at least one hour at 55° C., then filtered, being cooled to 35° to 40° C. in the process. They were then divided into smaller batches, the silver ion concentrations adjusted by appropriate additions of silver

[21] See p. 240 of paper referred to in footnote 3, p. 482.
[22] Davis, Sheppard, and Briefer, Ind. Eng. Chem., Analytical Ed., vol. 1, p. 56, 1929.

sulphate or potassium bromide solutions, and the emulsion coated as rapidly as possible. The maximum difference between any of the batches was 15 minutes, which, at a temperature not over 40°, introduced negligible changes in sensitivity; the temperature coefficient of afterripening is such that this interval at 40° corresponds to less than five minutes at 55°. These data may safely be considered to represent the direct effect of silver ion concentration on sensitivity, rather than the larger indirect effect which is the result of varying silver ion concentration during afterripening. The greatest effect was observed at hydrogen ion concentrations which very greatly retard afterripening.

Figure 7 presents results for a number of emulsions, all of the neutral ("C") type, with 4.0 mol per cent silver iodide. Speeds

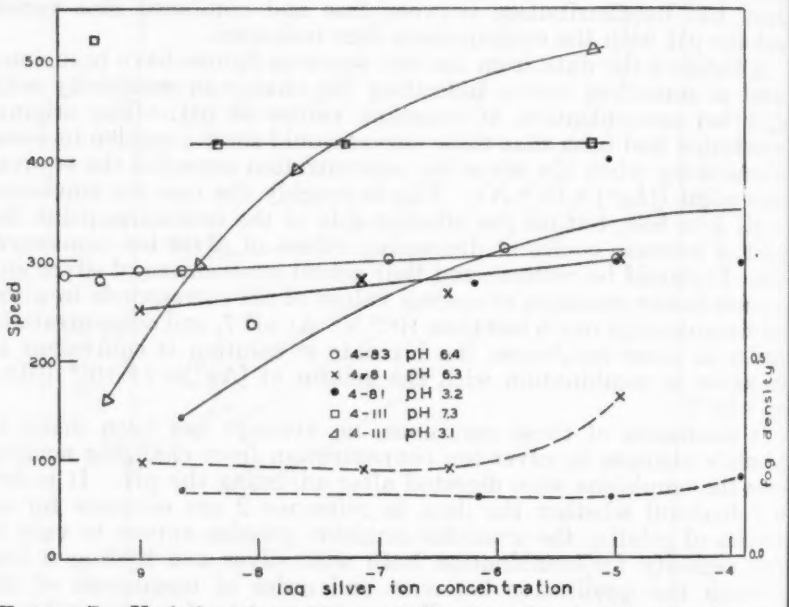

FIGURE 7.—*Variation of sensitivity and fog of emulsions with silver ion concentration at time of coating (after digestion under constant conditions)*

Solid lines, speed; dashed lines, fog.
○ Emulsion 4–83 at pH 6.4.
× Emulsion 4–81 at pH 6.3.
● Emulsion 4–81 at pH 3.2.
□ Emulsion 4–111 at pH 7.3.
△ Emulsion 4–111 at pH 3.1.

are derived from inertia values, γ being practically constant, except for emulsion 4–81 for which the minimum gradient value was more satisfactory. The normal range of silver ion concentrations in emulsions at coating is between $10^{-7.5}$ and 10^{-9}. The most striking feature of the data is the practically constant value of speed over an enormous range of silver ion concentration when the emulsions were at normal values of pH.

On the acid side of the isoelectric point the effect of silver ion concentration was much greater. As the figure is plotted on the basis of silver ion concentrations, the excess of silver over halogen at corresponding abscissas was less in the case of the batches on the

acid side of the isoelectric point, since the silver combined with gelatin was less. The difference between the neutral and acid batches would, therefore, be even greater if the results were presented in terms of excess bromide or silver.

Fog densities for 12-minute development of the different portions of 4–81 are also plotted in Figure 7, using dashed lines and the same symbols for the points as for the plot of speed of the corresponding portions. While there is a sudden increase in fog at the higher silver ion concentrations, not only excess of silver over bromine, but excess of free silver ions failed to produce large values of fog immediately; the batches with excess silver and normal pH deteriorated very rapidly, while those with excess silver at pH 3 were usable for over a month. The maximum fog in 4–111, made with ammonia-treated gelatin, was 0.06.

The marked effect of excess silver on the blackening of silver bromide without development, and the extension of spectral sensitivity toward the red reported by Fajans,[23] have both been studied mainly using silver bromide without protective colloid or protected by collodion, which does not have the capacity of gelatin to combine with silver ions. Tests were accordingly made with three emulsions 4-111, using both the neutral and acid batches, a similar emulsion: (4-110) available both with excess silver and bromide and having only 1 per cent AgI so that the sensitivity did not extend as far to the red as in 4–111, and an ammonia-process emulsion (1–166) with 4 per cent AgI.

The direct blackening was tested simply by exposing strips of corresponding pairs of plates (excess silver and excess bromide) to diffuse daylight, and observing the changes visually. The excess silver produced only a slight increase in the 4–110, and no appreciable difference in the 4–111 in either pair (pH 7.3 and 3.1).

TABLE 2.—*Distribution of silver and bromide ions in emulsion 4–81, on adjustment of pH and* $[Ag^+]$

[Results calculated to 1 liter of emulsion, containing 0.23 mol AgBr and 58 g gelatin]

pH	Added Ag^+ or Br^-	$[Ag^+]$	Excess in solution	Ag^+ combined with gelatin	Apparent change in adsorbed Br^- per mol AgBr
	g equivalent	*N*	*g equivalent*	*g equivalent*	*g equivalent*
6.3	0	7.4×10^{-8}	$1.23\times10^{-3}Br^-$	1.04×10^{-4}	0.
	$1.01\times10^{-3}Br^-$	1.05×10^{-9}	$8.8\times10^{-4}Br^-$	6×10^{-5}	$+1.7\times10^{-4}$.
	$2.3\times10^{-4}Ag^+$	3.9×10^{-7}	$1.8\times10^{-4}Br^-$	3.0×10^{-4}	-1.3×10^{-4}.
	$1.16\times10^{-3}Ag^+$	1.09×10^{-3}	$1.08\times10^{-3}Ag^+$	1.45×10^{-3}	-9×10^{-4}.
3.3	0	6.6×10^{-7}	$6\times10^{-7}Br^-$	3.6×10^{-5}	0.
	$1.01\times10^{-3}Br^-$	2.2×10^{-4}	$4.0\times10^{-4}Br^-$	3×10^{-6}	$+25\times10^{-4}$.
	$2.3\times10^{-4}Ag^+$	8.6×10^{-6}	$8.5\times10^{-4}Ag^+$	1.7×10^{-4}	-2.2×10^{-4}.
	$1.16\times10^{-3}Ag^+$	1.22×10^{-4}	$1.22\times10^{-4}Ag^+$	8.1×10^{-4}	-12×10^{-4}.

Spectral sensitivity was tested by exposure to a continuous source in a small grating spectrograph giving high intensity.[24] A Wratten "minus blue" filter was used to reduce the effect of stray light so that the exposure could be followed to regions of low sensitivity. The plates were brush developed to insure uniformity and measured with a microphotometer. No detectable change in spectral sensitivity

[23] See footnote 8, p. 483.
[24] Carroll and Hubbard, B.S. Jour. Research, vol. 4 (RP173), p. 692, 1930.

was produced by the excess silver in any of the sets compared. These same emulsions were also tested for a change in spectral sensitivity with pH, carrying the measurements well to the acid side of the isoelectric point of gelatin. The results were again negative with the possible exception of those batches of 1–166 containing excess silver; in this case the decrease in sensitivity for the longer wave lengths produced by decrease in pH from 7.7 to 3.2, if real, is of a smaller order of magnitude than the effect of changing from 4 to 1 per cent AgI.

In Table 2 the data are given for the adjustment of silver ion concentration in emulsion 4–81, which was made with the same sample of isoelectric gelatin used for the experiments on silver ion-gelatin combination. This emulsion was thoroughly washed with tap water, reaching a pH of 6.3 and $[Ag^+]$ of 7.4×10^{-8} N as given in the first horizontal row. Half of it was adjusted to pH 3.3 by the addition of sulphuric acid; each half was divided into four batches to which silver sulphate or potassium bromide solutions were added in the indicated quantities. The quantities of free ions in solution and of silver ions combined with the gelatin were calculated from the electrode readings and the data of Figure 3 of reference 2. The calculation may be illustrated by the figures in the second horizontal row. 1.01×10^{-3} g equivalent of bromide was added per liter of emulsion. The silver ion concentration, determined directly from the potential of the silver-silver bromide electrode, became 1.05×10^{-9}; the corresponding bromide ion concentration calculated from the solubility product was 8.8×10^{-4}. The solution, therefore, contains bromide in excess by $(8.8 \times 10^{-4}) - (1.05 \times 10^{-9}) = 8.8 \times 10^{-4}$ g equivalent per liter. At a pH of 6.3 and silver ion concentration 1.05×10^{-9}, we find from Figure 3 of reference 2 that 1×10^{-7} g equivalent of silver ion will combine with 1 g of gelatin, or 6×10^{-6} g equivalent with the 58 g in 1 liter of emulsion. The bromide in solution has, therefore, increased by $(8.8 \times 10^{-4}) - (1.23 \times 10^{-5}) = 8.7 \times 10^{-4}$ g equivalent over the original condition of the emulsion. The silver combined with the gelatin has decreased by $(1.04 \times 10^{-4}) - (6 \times 10^{-6}) = 0.98 \times 10^{-4}$ g equivalent from the original condition of the emulsion. These add up to 9.7×10^{-4} g equivalent. But 1.01×10^{-3} g equivalent of bromide was added. The difference is 0.4×10^{-4} g equivalent of bromide per liter ef emulsion, or 1.7×10^{-4} per mol of AgBr, which has apparently been removed by adsorption on the AgBr.

The sum of the changes in these quantities fails to agree with the addition in every case by an amount which is larger than the experimental error. If ascribed to changes in the bromide (or silver) ions adsorbed to the silver halide of the emulsion, the results are of the right sign and order of magnitude. Numerous calculations of this type indicate that approximate values can be obtained for adsorbed bromide, but it is obviously necessary to have data on the combination of silver ion with the gelatin in question to insure reliable results. Data from emulsion 4–83 in the higher bromide ion concentrations, and from emulsions 4–61 and 4–68 (reference 3) both give values for adsorbed bromide which fit the Freundlich equation within the limits of error, but the constants are quite different.

The increased effect of silver ion concentrations in acid emulsions is responsible for a curious effect which we have already mentioned.[25]

[25] Carroll and Hubbard, B. S. Jour. Research, vol. 1 (R P 20), p. 583, 1928.

This effect is further illustrated in Figure 8; the emulsions are described in Table 3. All were made with neutral silver nitrate solution; after mixing and ripening they were centrifuged and the silver halide suspended in dilute gelatin. The silver ion concentration of this suspension was next adjusted by addition of silver sulphate where desired, and it was then divided into portions, the pH of which was adjusted by sulphuric acid. The resulting range of silver ion concentrations is indicated in Table 3. These portions of the wash suspension, all containing the same excess silver or bromide and varying only in pH and the resulting distribution of silver ions, were then centri-

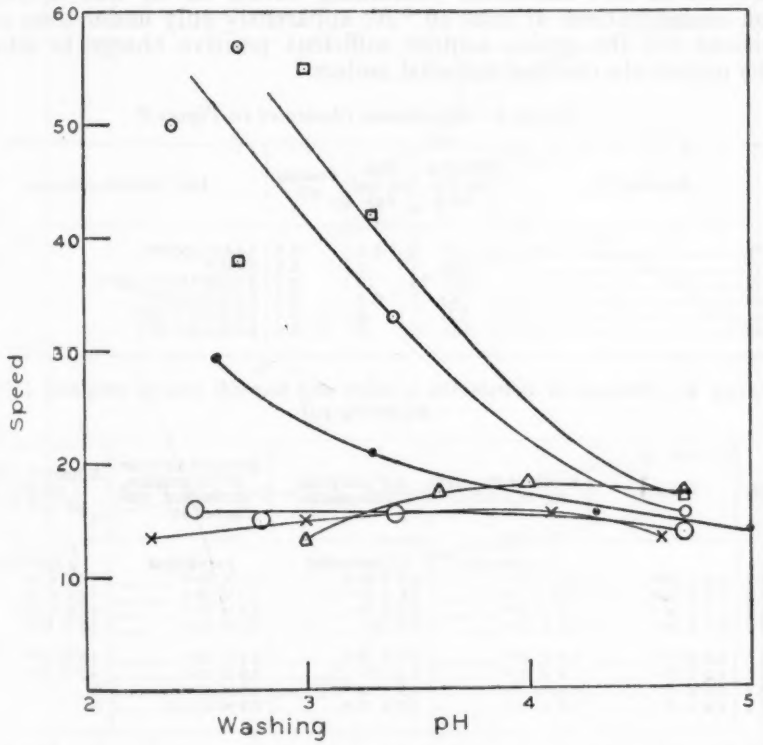

FIGURE 8.—*Variation of speed of centrifugally washed emulsions with pH of first resuspension*

fuged again and the silver halide suspended in fresh gelatin at constant pH. They were coated without digestion; other experiments showed that the effect tended to diminish on digestion, the after ripening bringing them to a common higher level of sensitivity. Ammonia-treated gelatin was used for the final suspension in all cases, to reduce fog in the emulsions with excess silver.

In the emulsions with excess bromide (6–80, 6–82) and in one with a small excess of silver (6–79), there was practically no effect produced by the changing pH of the wash suspension. In those with excess silver (6–76, 6–77, 6–81) there was a marked increase in sensitivity with increasing acidity. As the silver ion concentration of the wash suspensions increased with increasing acidity over the

range given in Table 3, there was a corresponding change in the final suspension, but it amounted to a maximum of 60 per cent, which could not account for the change in sensitivity. It is necessary to assume that a given silver ion concentration sensitizes the silver halide grains by an amount increasing with the acidity, most probably because there is increased adsorption of silver ions. A possible explanation will be discussed later in the paper. Entirely analogous results were obtained with ammonia process emulsions; illustrations are given by the "control" batches in Table 9 of reference 25. Colloidal silver and gold (reference 25) were found to sensitize only when introduced into emulsions containing excess silver, and hydrogen ion concentrations at least 10^{-3} *N;* apparently only under these conditions did the grains acquire sufficient positive charge to attract the negatively charged colloidal metals.

TABLE 3.—*Emulsions illustrated in Figure 8*

Emulsion No.	Symbol in Figure 8	Mol per cent AgI	Coating pH	[Ag⁺] in wash suspension
6-76	(.)	0.0	3.4	1.4 to 1.6×10^{-4}.
6-77	(O)	.0	3.4	6×10^{-4}.
6-79	(◯)	.0	3.4	4.7×10^{-4} to 4.4×10^{-3}.
6-80	(×)	2.3	3.4	3.1 to 3.5×10^{-10}.
6-81	(□)	.0	3.4	3.4 to 4.6×10^{-4}.
6-82	(Δ)	.0	8.2	3.5 to 4.2×10^{-4}.

TABLE 4.—*Changes in distribution of silver and bromide ions in emulsion 4-80 on adjusting pH*

pH	[Ag⁺]	Excess of Br⁻ over Ag⁺ in solution	Ag⁺ combined with gelatin	Excess of Ag⁺ over Br⁻ in emulsion, excluding adsorbed Br⁻	Apparent change in adsorbed Br⁻ per mol AgBr
		g equivalent	*g equivalent*	*g equivalent*	*g equivalent*
8.7	1.8×10^{-6}	5.0×10^{-3}	1.8×10^{-4}	1.3×10^{-4}	$+4.4\times10^{-4}$.
6.4	8.3×10^{-6}	1.10×10^{-3}	1.1×10^{-4}	1.0×10^{-4}	$+3.2\times10^{-4}$.
5.4	1.5×10^{-7}	5.8×10^{-3}	5.5×10^{-3}	4.9×10^{-3}	$+1.0\times10^{-4}$.
4.9	2.2×10^{-7}	4.0×10^{-3}	4×10^{-3}	3.6×10^{-3}	$+5\times10^{-4}$.
4.5	3.3×10^{-7}	2.5×10^{-3}	3.5×10^{-3}	3.2×10^{-3}	$+3\times10^{-4}$.
4.1	4.2×10^{-7}	1.8×10^{-3}	3×10^{-3}	2.8×10^{-3}	$+2\times10^{-4}$.
3.4	5.0×10^{-7}	1.35×10^{-3}	2.5×10^{-3}	2.4×10^{-3}	0.
2.2	6.4×10^{-7}	7.9×10^{-7}	2.5×10^{-3}	2.4×10^{-3}	0.

All results calculated to 1 liter of emulsion, which contained 0.24 mol AgBr and 60 g dry gelatin.

(b) HYDROGEN ION CONCENTRATION

Silver ion concentrations may readily be adjusted at constant pH, since small amounts of practically neutral salts may be used, but as already pointed out, change in hydrogen ion concentration involves a change in silver combined with gelatin and, therefore, a change in silver ion concentration. The smaller the amount of soluble bromide present in the emulsion the larger will be the change, both in relative and absolute units. Table 4 gives the results of changing the pH in an emulsion made with the standard de-ashed gelatin used for investigation of the silver ion-gelatin combination. This emulsion was thoroughly washed (six hours in running tap water) and contained only a very small excess of total halogen over silver. Changes in distribution of silver and bromide on changing pH have been calcu-

lated from the electrode readings and the data of Figure 3 of reference 2; values for adsorbed bromide are again only relative, the absolute amount being unknown. The change in adsorbed bromide is about what would be expected from the change in bromide ion concentration; the evidence is not sufficient to decide whether there is any effect of pH on the adsorption.

We have already [26] called attention to the fact that the change in silver ion concentration tends to oppose the direct effect of changing pH. When there is no subsequent afterripening, as in this case, the

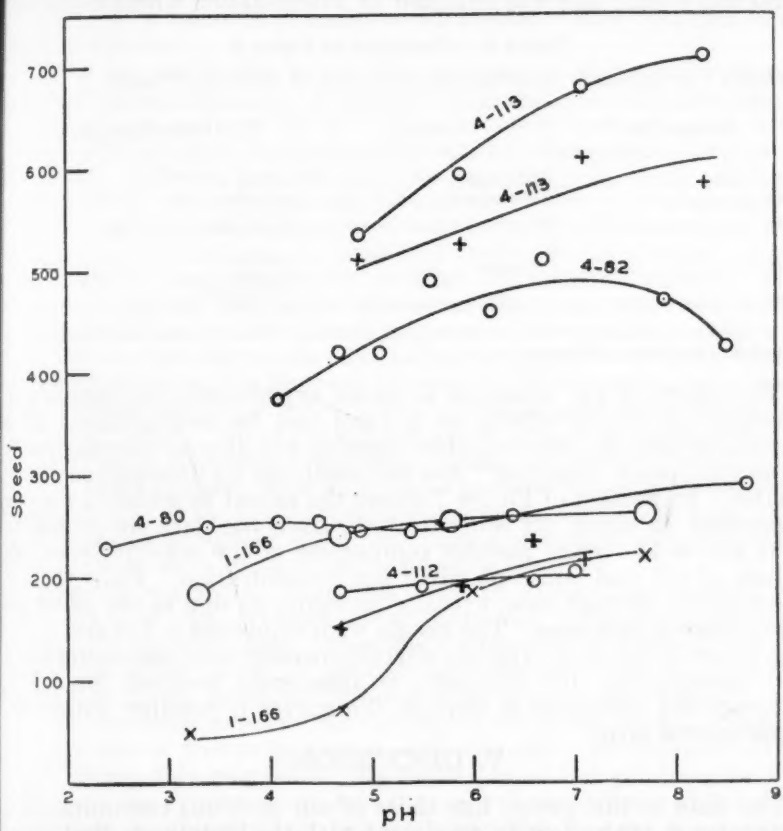

FIGURE 9.—*Variation of speed of emulsions with pH at time of coating (after digestion)*

change in silver ion concentration becomes relatively unimportant. In a thoroughly washed emulsion, such as 4–80, the silver ion concentration may change tenfold between pH 8.3 and 4.9. If, on the other hand, the emulsion contains about 1 per cent soluble bromide ($[Ag^+]$ approximately 10^{-9} *N*) the change in silver ion concentration may be as low as 20 per cent between the same limits of pH; as may be judged from inspection of Figure 7, this is quite negligible.

Figure 9 presents the results of changing pH of a number of emulsions just before coating. Three of the emulsions were divided in half,

[26] See p. 240 of footnote 3, p. 482.

and the silver ion concentration of each half adjusted before adjusting the pH. Most of the data are for thoroughly washed emulsions (indicated by circles), but three sets (indicated by crosses) are for emulsions containing about 1 per cent soluble bromide. The emulsions are described more fully in Table 5. The inertia of some of these emulsions tended to vary appreciably with the degree of development. Since the rate of development varied with the emulsion pH, as would be expected, the speeds are those for development to a constant value of γ (1.0 for emulsions 4–112 and 4–113 and 1–166; 1.5 for emulsions 4–80 and 4–82); this was obtained by interpolation where necessary.

TABLE 5.—*Emulsions in Figure 9*

Emulsion 1–166 was made by the ammonia process, the others by the neutral (C) formula.

Emulsion No.	Gelatin	[Ag^+] before adjustment of pH
4–80	De-ashed	8.3×10^{-8}.
4–82	Winterthur	6.7×10^{-8}.
4–112	do	7.7×10^{-9}.
		[1] 7.0×10^{-10}.
4–113	Ucopco	1.5×10^{-7}.
		[1] 7.5×10^{-10}.
1–166	do	[1] 8.3×10^{-10}.
		3.7×10^{-8}.

[1] Indicated by crosses in Figure 11.

The effect of pH observed in these experiments corresponds to Rawling's reversible effect; we did not test for reversibility. It is much less than the effect on after-ripening and almost vanishes under some conditions. Rawling [27] has demonstrated its dependence on the gelatin. Inspection of Figure 7 shows the extent to which it may be dependent on silver ion concentration, since the data for emulsions 4–81 and 4–111 make possible comparison of the sensitivity at two values of pH and constant silver ion concentration. Here the pH effect passes through zero, actually changing its sign as the silver ion concentration increases. The results with emulsions 4–112 and 1–166 (fig. 9) are of the same type, the effect increasing with decreasing silver ion concentration, but the order is apparently reversed for 4–113, although the difference in slope of the curves is possibly within the experimental error.

V. DISCUSSION

The data in this paper, like those of our previous communication (reference 3), are uniformly consistent with the hypothesis that after-ripening is the result of chemical reactions of the silver halide to form silver sulphide or possibly metallic silver. Such reactions must lead to the formation of acid and of halide ions, and should, therefore, be retarded by increase in bromide or hydrogen ion concentrations. This was found experimentally in every case. There is an apparent contradiction in the decrease of sensitivity in the emulsions with pH > 8, but it will be noted that the velocity of the change continued to increase, the maximum of sensitivity being reached in less time than for lower values of pH. The available evidence indicates that the quantity of silver sulphide is not the only variable in the effectiveness of a nucleus, so that photographic sensitivity might begin to fall off

[27] See footnote 5, p. 483.

even though the process of forming silver sulphide was not retarded. The effects of hydrogen and silver ion concentrations during digestion are thus as accountable as any features of the after-ripening process.

The effect of environment pH is apparently independent of previous afterripening, since Rawling found it to be independent of the presence of nuclei formed by known additions of allyl thiocarbamide. It must be explained by hypotheses which do not involve changes in the nucleation of the grains. We have an analogous case in the mechanism of spectral sensitization, since Sheppard [28] found that the relative spectral sensitivity of a given emulsion-dye combination was not affected by addition or removal of nuclei which produced great changes in the total sensitivity.

It will be useful first to consider the nature of the adsorption of gelatin to silver bromide. Reinders [29] demonstrated that the adsorption of gelatin reduces the adsorption of other materials, but it has been tacitly assumed in many cases that the adsorption of ions and of protective colloids had distinct mechanisms and were relatively independent. According to the "Zwitterion" theory of ampholytes,[30] however, gelatin is considered to be very largely in the ionic state, even though most of the ions (or micelles) are externally neutral because they carry an equal number of positive and negative charges. Such zwitterions should be capable of oriented polar adsorption to a crystal lattice like silver bromide; assuming the existence of amino acid groups the gelatin zwitterion would be adsorbed to silver ions of the surface by electrostatic attraction between Ag^+ and $-COO^-$, and to the bromide ions by their attraction for $-NH^+_3$. Undissociated molecules would not be adsorbed. The externally charged ions of the earlier theory, which exist in increasing proportions as the pH departs from the isoelectric point in either direction, would be adsorbed only to the corresponding ions of the silver bromide surface. In every case, adsorption of the gelatin should be polar, and competitive with the adsorption of other ions, even those of silver bromide itself.

It seems reasonable that this type of adsorption explains the superiority of the proteins over un-ionized colloids as protective colloids for silver bromide, expecially with regard to protection of the unexposed silver bromide against development if we assume that adsorption of the developer ion is the first step in that process.

The zwitterion concept also implies a relatively rapid change in the number of free NH_2 groups with the pH. As pointed out by Slater Price, this may effect the reactivity of the gelatin with bromine. It also appears to explain the marked dependence of the silver ion-gelatin combination on pH, assuming this to take place at the amino group, much better than the opening of peptide linkages which are assumed in our previous discussion of this subject [31] or the structural changes suggested by Sheppard (reference 13).

We believe that our results may best be explained on the assumption that gelatin is adsorbed to silver halides in preference to all other materials present. Only the bromide ion (which is adsorbed more strongly than the silver ion) will also be appreciably adsorbed, especially in acid solutions where the acid dissociation of the gelatin is reduced so that the $-COO^-$ ion groups are less available for

[28] Sheppard, Colloid Symposium Monograph, vol. 3, p. 3.
[29] Reinders, Zeit. f. phys. Chem., vol. 77, p. 677, 1911.
[30] Bjerrum, Zeit. f. phys. Chem., vol. 104, p. 147, 1923.
[31] See footnote 2, p. 482.

adsorption to the Ag^+ ions of the crystal lattice. Our data in agreement with the work of Slater Price and his associates show that the effect of hydrogen ion concentration on sensitivity is greater at higher bromide ion concentrations. As is evident from Figure 7, this may better be expressed that at low values of pH, bromide has an increased desensitizing effect. It has already been mentioned that under these conditions it should be more capable of displacing adsorbed gelatin, with consequent desensitization. Silver ions will, in general, be adsorbed in appreciable quantity only at relatively high concentrations. (It will be remembered that the silver ion concentration in an emulsion at normal values of pH exceeds the bromide ion concentration only when the emulsion contains about 0.4 per cent excess silver.) Our most direct evidence for this is the independence of the spectral sensitivity of the silver and hydrogen ion concentration. There was no indication that even the considerable excess of silver present in some of the emulsions caused an increase in sensitivity to the longer wave lengths. There is, furthermore, evidence that the adsorption of the gelatin causes such a shift, since the sensitivity of pure silver bromide in gelatin has its maximum at about 450 $m\mu$ as against 420 $m\mu$ for silver bromide collodion[32]; Eder's sensitivity curves show an unmistakable shift of the whole curve to the red in the presence of gelatin. It is therefore probable that in the grains of a silver bromide-gelatin emulsion the deformation of the external bromide ions of the crystal lattice is already accomplished so that it is unaffected by silver or hydroxyl ions at moderate concentrations.

The effect of excess silver on the sensitivity of gelatin emulsions has been found to be unexpectedly small in view of its marked effect under other conditions, such as the photolysis of medium-free silver bromide. The most important factor is the combination of gelatin with silver ions, which retards the increase of silver ion concentration when soluble silver salts are added to an emulsion, and prevents the formation of the "silberkorper" of Fajan's experiments. There is a further influence to be considered. In the photolysis of medium-free silver bromide excess silver increases the rate of reaction under constant illumination by a factor of several times, although the increase in absorption of light can be detected only by careful measurement. This result can not be explained wholly by the change in the primary photochemical process; the silver must also influence secondary reactions, probably by acting as a bromine absorbent. Some bromine absorbent is essential to prevent regression in the photolysis of pure silver bromide. In the emulsion, the case is quite different, and an absorbent as inefficient as a silver salt does not add to sensitivity. The evidence indicates that some more effective material is normally present, and that the effects of such variables as hydrogen ion concentration are to be explained in terms of some secondary reaction, probably connected with the bromine liberated during exposure.

This is the basic hypothesis used by Slater Price [33] to explain the effect of pH on sensitivity. We fully agree with him that the photochemical reaction leading to the latent image, like practically every other photochemical reaction which has been studied, involves a primary process which is the direct consequence of the absorption of

[32] Vogel, Eder's Ausführliches Handbuch der Photographie, vol. 3, p. 143, 5th ed., 1903. Eder, Handbuch, vol. 2, Figure 162, p. 377; 1st ed., 1897.
[33] See footnote 10, p. 484.

light, and subsequent secondary reaction or reactions which are purely chemical in nature. The secondary reactions are subject to the same influences as other chemical reactions, and consequently the total chemical reaction associated with a given primary absorption may be widely modified by changing conditions such as the pH. There have been statements that in the photographic emulsion the primary and secondary reactions are the formation of the latent image and development, respectively. While this statement may be a useful analogy in the discussion of photochemistry, it is pure assumption that the formation of the latent image involves only the primary process; there is no evidence that such is the case. A priori it is highly improbable that in a system as complicated as the photographic emulsion there are no secondary reactions, and the existence of the intermittency and reciprocity effects are strong evidence that the secondary reactions do occur. The quantum theory of photochemical reactions implies that the primary process is the necessary consequence of the absorption of a quantum of the proper frequency; a change in the quantum yield with constant absorption, as in exposures at different intensities, must, therefore, be ascribed to secondary reaction.

The shift in spectral sensitivity observed by Fajans involves the primary process, since a smaller quantum has become effective. In contrast to this, the increase in atoms of silver liberated, over and above the increased quantum absorption, must mean a change in the secondary reactions—decreased regression, for example.

While the existence of secondary reactions in latent image formation is practically necessary in the light of general photochemistry, there is no direct evidence of their chemical nature. Slater Price adopts the most obvious chemical theory—that the secondary reactions are connected with the disposal of the bromine liberated by photolysis of silver bromide. In some form or other this theory has been used since the earliest days of gelatin emulsions to explain their superior sensitivity. The gravest objection to it is the general failure of halogen absorbents to act as photographic sensitizers in gelatin emulsions. Materials such as thioanilides [34] and sulphites,[35] even though they are halogen absorbents and may be adsorbed to silver bromide so as to be in the most favorable position for reaction with the bromine, are found to be desensitizers. However, they greatly accelerate the visible photolysis of silver bromide, and delay or prevent solarization. It is, therefore, necessary to assume that silver bromide-gelatin emulsions normally contain something which as an absorbent for the very small quantities of bromine which are liberated in the formation of latent image corresponding to a working density is more efficient than any of the materials which may be added. It must be present only in minute amounts or have only a small capacity, because it can be supplemented by other halogen absorbents for the longer exposures corresponding to solarization and direct blackening. Slater Price believed this to be the gelatin, and demonstrated the parallel between the effect of varying hydrogen ion concentration on the reactivity of bromine and gelatin on the one hand and the sensitivity on the other. The capacity factor just mentioned was not discussed, but it might have been explained by assuming that only

[34] Sheppard and Hudson, Phot. J., vol. 67, p. 359, 1927.
[35] Sheppard and Wightman, Phot. J., vol. 69, p. 83, 1929.

the gelatin in immediate contact with the grain can react rapidly enough to be effective.

Admitting the existence of an efficient bromine absorbent in silver bromide-gelatine emulsions, we believe that consideration of all the evidence favors Hickman's[36] hypothesis that it is silver sulphide. It does not seem necessary to accept Hickman's further hypothesis that the reaction leads to increased liberation of metallic silver; it is sufficient if we assume that it merely prevents regression, since the quantum yield for the photolysis of silver bromide in photographic emulsions is more probably less than one, rather than greater than one. The silver sulphide is present in quantities of the right order of magnitude to correspond to the capacity observed. On the hypothesis that the silver sulphide nuclei orient[37] the photolysis of the silver bromide, they may become preferred bromine absorbents merely by virtue of position, and the orientation hypothesis may be retained even though the latent image is explained in terms of structure of photolytic silver rather than quantity.

The behavior of highly disperse (Lippman type) emulsions offers an apparently crucial distinction between gelatin and silver sulphide as bromine absorbents. The silver bromide of these emulsions has a maximum specific surface for adsorption of gelatin. They have had a minimum of ripening and, therefore, contain a minimum of silver sulphide. Lüppo-Cramer[38] has furnished quantitative data showing that in these emulsions, unlike ordinary types, the developable sensitivity may be increased by halogen absorbents, such as nitrite and bisulphite. This indicates that the normal bromine absorbent is absent, so that the silver sulphide rather than the gelatin must normally have this function.

It is probable that atomic bromine reacts directly with silver sulphide, if at all; the calculations of Lambert and Wightman[39] indicate that this gives a larger decrease of free energy than if water is involved, as well as being more rapid. However, if we assume that the reaction involves water, the effect of hydrogen ion concentration may still be explained by its effect on the hypobromous acid equilibrium, as calculated by Slater Price. Otherwise, as the reaction between atomic bromine and silver sulphide would not be directly affected by hydrogen ion concentration, there could only be an indirect effect through reaction of gelatin with the by-products of the first reaction.

This discussion has been based on the commonly accepted theory that the latent image is the result of the photolysis of silver bromide. Weigert[40] has recently advanced a "micellar" theory of the latent image which is receiving serious consideration because it is based on his important contributions to the photographic effects of polarized light. He postulates that the latent image is the primary product of the absorption of several quanta by a micelle of silver or silver sulphide, the micelle being raised to a higher energy level which is stable until the energy is used to activate the developer. Regression and such phenomena as the intermittency and reciprocity effects are explained by a secondary reaction, the "inner development" of the

[36] Hickman, Phot. J., vol. 67, p. 34, 1927.
[37] Sheppard, Trivelli and Loveland, J. Franklin Inst., vol. 200, p. 51, 1925.
[38] Lüppo-Cramer, Zeit. f. wiss. Phot., vol. 30, p. 201, 1931; and earlier articles.
[39] Lambert and Wightman, J. Phys. Chem., vol. 31, p. 1249, 1927.
[40] Weigart, Zeit. f. Wiss. Phot., vol. 29, p. 191, 1930.

micelle by the medium, whereby the energy is lost and no longer available to start development. The secondary reaction being exclusively a regression effect, increase in pH, which would tend to increase the reduction potential of the gelatin and the tendency to inner development should decrease rather than increase sensitivity. The effect of silver ion concentration would be difficult to predict.

We conclude that under normal conditions in the photographic emulsion the adsorption of gelatin to the silver bromide grains is such as to reduce the adsorption of other materials and their consequent effects on sensitivity. Replacement of adsorbed gelatin by bromide ions, which causes desensitization, is favored not only by increased bromide ion concentration, but also by increased hydrogen ion concentration. All effects of environment on photographic sensitivity which do not involve changes in absorption of light must be explained in terms of secondary reactions in latent image formation. The most obvious of these secondary reactions, the elimination of bromine, is better explained by reaction with silver sulphide rather than with gelatin.

VI. Acknowledgment

In the making and testing of the emulsions described in this paper C. M. Kretchman rendered valuable assistance.

WASHINGTON, February 15, 1932.

CAPACITANCE AND POWER FACTOR OF A MICA CAPACITOR AS MEASURED AT THE BUREAU OF STANDARDS AND THE NATIONAL PHYSICAL LABORATORY

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ABSTRACT

A mica capacitor has been transported on four occasions between the Bureau of Standards and the National Physical Laboratory. Seven sets of measurements of capacitance and power factor were made on the capacitor, five at the Bureau of Standards and two at the National Physical Laboratory. During the first transportation changes occurred in the capacitance, which make the results of little value. No certain changes occurred during subsequent transportations.

The principles underlying the methods of the two laboratories are quite different At the Bureau of Standards the mica capacitor was compared by alternating current with an air capacitor, the capacitance of which can be determined in terms of resistance and time. At the National Physical Laboratory the mica capacitor was compared by alteranting current with a mutual inductance, the value of which can be computed from its dimensions. Results show that the two methods give values in good agreement. The measured capacitances agree to 1 or 2 parts in 10,000, which is about the accuracy of the measurements.

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I. INTRODUCTION

In November, 1927, an agreement was reached to undertake some intercomparisons of the capacitance and power factor of a mica capacitor. A subdivided mica capacitor selected for this comparison was calibrated alternately at the Bureau of Standards and the National Physical Laboratory by the methods regularly used in the two laboratories. This comparison has extended over a period of more than three years. The capacitor was first carried from Washington to Teddington by a special messenger. The three subsequent transits were made by parcel-post shipment.

The results show that the values of the international microfarad as maintained at the two laboratories are the same within the limits of the present intercomparison.

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II. THE CAPACITOR

The mica capacitor chosen for intercomparison was a subdivided one purchased by the Bureau of Standards about 1917 and designated as B. S. 16390. It consists of eight sections, the sections being designated according to their capacitances as 0.01, 0.02, 0.02′, 0.05, 0.1, 0.1′, 0.2, and 0.5 The sum of the three smallest sections connected in parallel is designated as Σ0.05, of the four smaller sections as Σ0.1, and the sum of all eight sections as Σ1.0. From the time of acquisition until these comparisons were undertaken this capacitor had been subjected to ordinary laboratory service at normal room temperatures. Occasional calibrations during this period showed that both the capacitance and power factor were approximately constant. It, therefore, seemed well suited for the intercomparison. Each section of the capacitor is constructed from sheet mica interleaved with tinfoil, the completed section being impregnated with paraffin and clamped between brass plates about 4 mm thick. The distance between individual sections is about 2 cm. The two terminals of each section are brought out to individual binding posts mounted on a hard-rubber top. The clamping plates are not connected to either terminal. There is no shield to the individual sections nor to the capacitor as a whole, the container being a wooden box.

III. TIMES OF SHIPPING AND MEASURING THE CAPACITOR

The capacitor was measured at the Bureau of Standards in April, 1928. In July, 1928, it was sent to the National Physical Laboratory, where measurements were made in January, 1929. It was returned to the Bureau of Standards in the spring of 1929, where it was measured in June, 1929, and again in January and February, 1930. In May, 1930, it was again sent to the National Physical Laboratory, where measurements were made in September of that year. It was returned to the Bureau of Standards in the fall of 1930, a set of measurements made in March 1931, and the final set of the series made in February, 1932.

IV. CONDITIONS UNDER WHICH MEASUREMENTS WERE MADE

At both laboratories the temperature of the capacitor was maintained during measurement at 25° C. ±0.1° C. The first measurements at each laboratory were made at four frequencies, namely, 60, 100, 1,000, and 2,000 cycles per second; subsequent measurements were made at 60 and 1,000 cycles only. In all cases the air pressure was the barometric pressure at the laboratory. It is improbable that the differences in the barometric pressure caused either by the relative altitudes of the two laboratories or by the ordinary variations will produce a change in capacitance greater than 1 part in 10,000.[2]

[2] The pressure variation caused by the difference in altitude is about 1 cm of Hg. The maximum variation at any one place is about 5 cm of Hg. A mica capacitor usually changes about 0.2 parts in 10,000 per centimeter change in pressure. See Bul. B. S., vol. 6, p. 459, 1911.

V. METHOD OF TESTING AT THE BUREAU OF STANDARDS

The method of testing a capacitor of unknown value at the Bureau of Standards is to compare it, either directly or indirectly, with an air capacitor, the value of which has been determined in terms of resistance and time. The comparison between the unknown and the air capacitor is made with alternating current of the desired frequency, the assumption being made that the capacitance of the air capacitor is independent of the method of measurement and that its power factor is zero.

1. AIR CAPACITOR

The bureau possesses a bank of fixed air capacitors so arranged that any capacitance between 0.01 μf and 0.26 μf can be obtained in the 0.5 μf section of the unknown with the five 0.1μf capacitors connect- steps of 0.01 μf. Hence seven sections of the mica capacitor were compared directly with air capacitors of the same nominal values, while only in the case of the 0.5 μf section and the sum of all the sections was an indirect comparison necessary. The most satisfactory scheme for obtaining values of the 0.5 μf section was to compare the capacitance and power factor of each of five 0.1 μf standard mica capacitors with an air capacitor of the same value; then to compare ed in parallel. To obtain a standard of 1.0 μf with which to compare all the sections of the unknown connected in parallel, two standard mica capacitors each having a nominal value of 0.5 μf were first compared with the five 0.1 μf mica capacitors connected in parallel, then these two 0.5 μf capacitors were used in parallel to give the required 1.0 μf standard.

The accuracy which can be attained by the indirect comparison with an air capacitor as described above can be judged by the values for the Σ sections as given in Table 4. For the Σ 0.05 and Σ 0.1 μf sections, the measured value of each was obtained by direct comparison with an air capacitor, while the computed value was obtained by the summation of the measured values of the individual sections. The measured value of the Σ 1.0 μf section was obtained by the method as described using mica standard capacitors, whereas the computed values of the same Σ section were obtained by summing the values of the separate sections as independently obtained. This method is less satisfactory for small values of capacitance than for large values, since the greatest source of error is caused by the capacitance of the leads; the smaller the capacitance of the section, the greater the percentage of error. For the Σ 1.0 μf section the maximum difference between the measured and the computed values of the capacitance is 2 parts in 10,000, while for the power factor the maximum difference is 1×10^{-4}. For the Σ 0.1 μf section the differences between the measured and computed values are approximately the same as for the Σ 1.0 μf section, while for the Σ 0.05 μf section they are somewhat larger.

2. ALTERNATING-CURRENT BRIDGE

The method used for the comparison of capacitance is the series-inductance bridge of Rosa.[3] For comparisons at 60 and 100 cycles per second a vibration galvanometer was used as the detecting instru-

[3] This bridge was first described by Grover, Bul. B. S. vol. 3, p. 389, 1907. The form now used in the laboratory is described by Curtis, Bul. B. S. vol. 6, p. 435, 1911.

ment. For frequencies of 1,000 and 2,000 cycles per second a telephone receiver was used for the detector. In measuring capacitances of 0.2 μf and smaller a bridge of three branches was used, one of which had a ground[4] connection at the galvanometer terminal. A substitution method was employed in all measurements. A diagram of the bridge is given in figure 1. One terminal of the detector, G, is permanently connected to point, A, on the first branch of the bridge. The second terminal, by means of the double-throw switch, can be

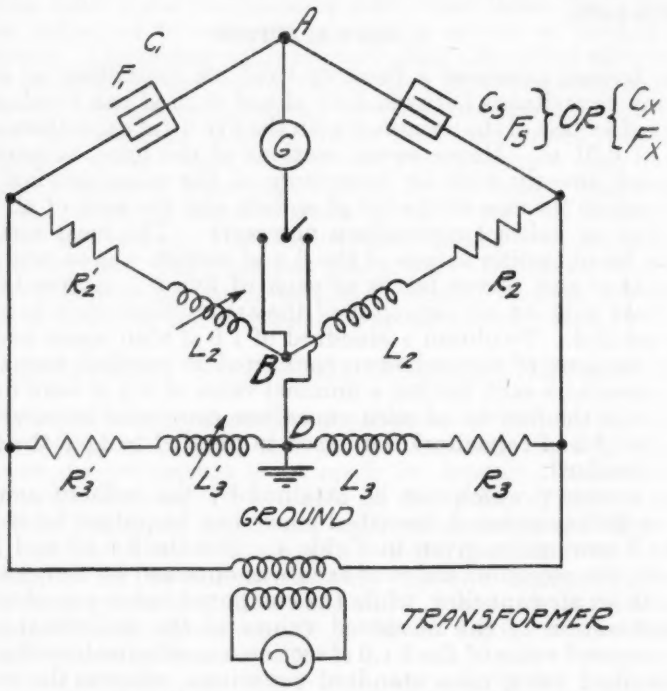

FIGURE 1.—*Diagram of a. c. bridge used at the Bureau of Standards for comparing capacitors*

C_1, auxiliary capacitor having capacitance C_1 and power factor F_1.
C_s, standard capacitor having capacitance C_s and power factor F_s.
C_x, test capacitor having capacitance C_x and power factor F_x.
G, detector.
R and L)with subscript and superscript), total resistance and total inductance, respectively, of the designated arms.

connected to either points B or D of the second and third branches, respectively. With the standard capacitor C_s in the bridge and an auxiliary capacitor C_1 having the same nominal value of the capacitance, the resistance of R'_2 (including the resistance of the inductor L'_2) is made numerically equal to some decimal multiple of the value of C_s. The detector is connected to B and a balance obtained by adjusting the resistance R_2 and the inductor L'_2. The detector is then connected to D and R'_3 and L'_3 adjusted for a balance. The detector is again connected to B and, if necessary, a new adjustment made for a balance. This shifting from one arm to the other with

[4] This is a method proposed by K. W. Wagner, Elekt. Zeit. vol. 32, p. 1001, 1911.

consequent balancing is continued until changing the connection does not require a change in balance. Then, provided the ratios L_2/R_2 and L'_2/R'_2 are both small, the equation connecting capacitances and resistances is

$$C_1/R_2 = C_s/R'_2$$

and the equation for computing the power factor is

$$F_s - F_1 = \omega\ (L_2/R_2 - L'_2/R'_2)$$

Now the standard capacitor C_s is replaced by the unknown capacitor C_x. The bridge is now balanced by adjusting R'_2 (not R_2 as when the standard is in the bridge) and L'_2 to have the values R''_2 and L''_2, and by adjusting R'_3 and L'_3, using the same method as for the standard. Now

$$\frac{C_1}{R_2} = \frac{C_x}{R''_2}$$

and

$$F_x - F_1 = \omega\left(\frac{L_2}{R_2} - \frac{L''_2}{R''_2}\right)$$

Combining these with the equations when the standard is in the bridge

$$C_x = R''_2 \frac{C_s}{R'_2}$$

and

$$F_x - F_s = \omega\left(\frac{L'_2}{R'_2} - \frac{L''_2}{R''_2}\right)$$

Since R'_2 was made a decimal multiple of C_s, the equation shows that C_x is the same decimal multiple of R''_2, thus simplifying the computation. When C_s is an air capacitor, F_s is assumed to be zero.

The substitution method does not require an accurate knowledge of the values of the resistances, since only the ratio R'_2/R''_2 enters in the final computation. If in the change of the resistance from the value R'_2 to R''_2 only coils of small value are inserted or removed, a calibration of the resistances to a high relative accuracy is not necessary to give a precise value of the ratio of the two capacitances.

3. ABSOLUTE CAPACITANCE BRIDGE

To obtain the capacitance values of the air capacitors, measurements are made in terms of resistance and time by Maxwell's method.[5] In this method a ballistic galvanometer is used to compare a constant current flowing in one direction through the galvanometer with the integral value of a current in the opposite direction produced by the series of charging currents when a capacitor is charged and discharged at a rapid rate. The assumption is made that the standard air capacitors of the Bureau of Standards have the same capacitance under all methods of measurement herein employed, this being sup-

[5] For details of using the method at the bureau, see paper by Curtis and Moon, B. S. Sci. Papers, vol. 22, p. 487, 1927.

ported by the fact that they have the same capacitance when measured with 100 charges and discharges per second as with 1,000 charges and discharges per second.

It is possible to obtain by this method results accurate to a few parts in a hundred thousand. However, to obtain that accuracy, great care must be exercised in the calibration of the resistance arms of the bridge and in the measurement of the number of charges and discharges per second of the capacitor. The highest order of accuracy was not attempted in the measurements herein reported. There is a possibility of an error of 1 or 2 parts in 10,000 from uncertainty in the values of the resistances and a somewhat smaller error from the time measurements.

VI. METHODS OF TEST AT THE NATIONAL PHYSICAL LABORATORY

At the National Physical Laboratory, measurements of capacitance are made by a direct comparison with the standards of mutual inductance and resistance. The value of the primary standard of mutual inductance is obtained in centimeters by calculation from its dimensions, and the determination of capacitance is thus an absolute measurement, since the values of the resistance standards are also known in c. g. s. units. The values of capacitance are, therefore, obtained in absolute microfarads. For practical purposes it is important that the unit of capacitance shall be consistent with the unit of resistance and since it is known that

$$1 \text{ international ohm} = 1.0005 \text{ ohms (c. g. s.)}$$

the results of the capacitance measurements are converted to international units by the use of the relation

$$1\ \mu\text{f (absolute or c. g. s.)} = 1.0005 \text{ international microfarad}$$

1. PRIMARY STANDARD OF MUTUAL INDUCTANCE

The primary standard mutual inductor of the National Physical Laboratory has been described in previous papers.[6] For the present purpose it is sufficient to state that the primary coil consists of a single layer solenoid wound in two sections on a marble cylinder; the secondary coil is larger in diameter than the primary and contains many more turns (about 500). This design was adopted as giving an inductance of convenient value for most purposes (10 mH), in a form which is as permanent as possible, and on which it is possible to obtain the highest accuracy in the determination of the linear dimensions, and the calculation from them of the mutual inductance. This calculated value of the mutual inductance is only realized in practice when the frequency of the alternating current supplied to the instrument is so low that the effects of capacitance in and between the windings are negligibly small. It will, however, be evident that the effects of capacitance will be comparatively large in a standard of this form, owing to the large size of the secondary coil, and it is, therefore, impossible to use the primary standard itself in precision work at

[6] A. Campbell, N. P. L. Collected Researches, vol. 4, p. 213; or Proc. Roy. Soc. A., vol. 79, p. 428, 1907; also Proc. Roy. Soc. A. vol., 87, p. 391, 1912.

telephonic frequencies. Secondary standards, designed to have smaller capacitance effects, and also to be continuously variable and direct reading are, therefore, used for alternating current bridge work. These are calibrated in terms of the primary standard at a frequency of 10 cycles per second, at which frequency the capacitance effects on the primary standard are known to be of the order of 1 part in 1,000,000.

2. WORKING STANDARDS OF MUTUAL INDUCTANCE

The mutual inductors used in alternating current bridge work at the National Physical Laboratory take the form of the Campbell inductometer.[7] The instrument used for this work covered the range 0 to 11 mH, so that the reading 10 mH could be measured against the primary standard by a simple direct comparison at the frequency of 10 cycles. The range of the instrument is subdivided into hundredths by means of two successive decade dials, and further subdivision is obtained by including in the secondary winding a small moving coil, carrying a pointer which moves over a scale graduated in microhenries of mutual inductance. The instrument could be read to the nearest 0.1 μH at any point of its range; that is, to an accuracy of 1 part in 100,000 of the total value. The accuracy of subdivision is checked as follows: By the fitting of a special switch to the decade dials, the various tenths into which each dial is divided are compared with one another, and thus each is determined in terms of their sum. The comparison of the various tenths is made by simple substitution in a circuit which allows any one of them to be balanced against a fixed mutual inductance of about the same value, the small moving coil of the instrument being used to take up the differences. The same process is applied to the second decade dial. The scale of the moving coil is calibrated by the use of Albert Campbell's device of the 10-strand cable; that is, an auxiliary mutual inductance adjustable in value is obtained by means of two coils, one of which is wound with a cable of 10 strands well twisted together. The 10 strands are connected in series, and the junctions are brought to the studs of a decade dial, so that between studs O and n there are n strands in series. The dial having been set at stud 10, the value of the mutual inductance is adjusted by moving one of the coils bodily until the total mutual inductance exactly balances the mutual inductance which is to be subdivided. Tenths of this value are than obtained by taking the intermediate settings of the dial. The accuracy of the subdivision may be increased as required by arranging the coils to be farther apart. All the readings required in the calibration are taken on the scale of the small moving coil of the inductometer, which is always included in the circuit.

It will be observed that all the calibrations depend on the principle that mutual inductances between several secondary coils and a common primary are additive. The principle assumes that capacitance effects are negligible, and care is taken to ensure that this is so, by the use of low frequency (100 cycles or less) for all such calibrations.

When the above-mentioned calibrations have been carried out, the value of the low-frequency or geometrical mutual inductance of the instrument is known for every reading, but when the instrument is

[7] A. Campbell, Proc. Phys. Soc., vol. 21, p. 69, 1908.

used at frequencies greater than 100 cycles, allowance must be made for the effects of capacitance and eddy currents in the windings. As a result of these effects, the secondary voltage V_s of the instrument is not exactly in quadrature with the primary current I_p, and is not simply proportional to the frequency and the value of the geometrical inductance M_o. Instead of the simple ideal equation $V_s = j\omega M_o$, we must write

$$V_s = [\sigma + j(M_o + \Delta M)\omega] I_p$$
$$= [\sigma + j M\omega] I_p$$

where σ and ΔM are correcting terms representing the effects of capacitance and eddy currents. These are called for convenience the "impurity" and "frequency correction," respectively, of the instrument at the reading M_o and the frequency $\omega/2\pi$. The quantity $M_o + \Delta M = M$ is called the "effective mutual inductance" of the instrument and the small angle $\tan^{-1}\frac{\sigma}{M\omega}$ is called, for obvious reasons, its "phase defect."

The values of the phase defect and frequency correction of the secondary standard inductors are determined by comparing them at several frequencies covering the working range, with mutual inductors wound of highly stranded wire in such a manner that capacitance and eddy currents effects are reduced to a minimum. Their design is identical with that used for standard inductors for radio-frequency work, and the effects of capacitance in them are actually deduced from measurements of their self-capacitance at radio-frequencies.[8]

Two other properties of the secondary standard inductors are of importance for capacitance measurement; the self-inductance and resistance of the fixed or nonadjustable winding. The geometrical or low-frequency value of this self-inductance, L_o, is measured in terms of the mutual inductance by means of the Heaviside bridge in the form developed by Albert Campbell.[9] The low-frequency value of the resistance p is determined by a simple direct-current measurement. When the working frequency exceeds 100 cycles, these quantities also must be corrected for the effects of capacitance and eddy currents in the windings which manifest themselves as an increase in the effective values of the inductance and resistance. The effective self-inductance becomes $L_o + \Delta L$, and the effective resistance $p + \Delta p$. The small correcting terms ΔL and Δp are determined by a comparison of the coil, at the required frequencies, with a standard inductor of the type used as standards in radio-frequency work. The effects of capacitance and eddy currents are reduced to a minimum in such standards, and may be estimated with sufficient accuracy from the results of measurements of self-capacitance and effective resistance at radio frequencies.

3. CAREY FOSTER BRIDGE FOR MEASUREMENTS OF CAPACITANCE AND POWER FACTOR

The actual measurement of capacitance in terms of mutual inductance and resistance is made by means of the Carey Foster bridge, in a form adapted to the requirements of precision alternating-current

[8] L. Hartshorn, Proc. Phys. Soc., vol. 38, p. 307, 1926.
[9] A. Campbell, Proc. Phys. Soc., vol. 21, p. 69, 1908.

work. A complete account of the method as used at the present time has not hitherto been published, but notes on certain of the essential features have been given by A. Campbell,[10] S. Butterworth,[11] and D. Dye.[12]

The circuit now used is shown in Figures 2 and 3, of which Figure 2 shows the electrical network in its simplest form, and Figure 3 gives the actual arrangement of the apparatus used. The bridge proper consists of the network *FABD*, which is supplied with alternating current from the triode oscillator *O*. The detector of balance *G* is a telephone receiver or Campbell vibration galvanometer, depending on the frequency at which the measurements are to be made. *M* is the standard variable mutual inductor described above, of which *FA*

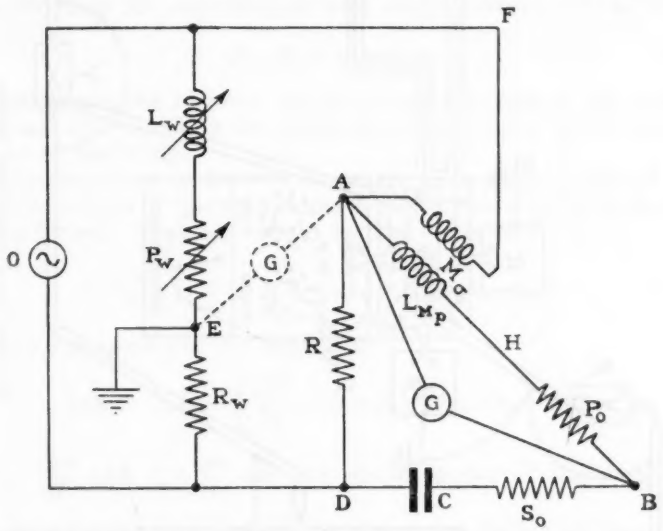

FIGURE 2.—*Carey Foster bridge for the measurement of capacitance and power factor; simplified circuit diagram*

C, capacitor under test.
M, standard variable mutual inductor.
P_o, *R*, fixed resistors.
S_o, variable resistor.
L_w, P_w, *E*, R_w, Wagner earth connection.

is the adjustable winding, and *AH* the fixed winding. P_o, *R*, and S_o are nonreactive resistors which take the following forms. P_o and *R* are fixed resistance coils of various sizes, oil-immersed, and electrostatically shielded by brass containers. S_o is a nonreactive resistance box capable of fine adjustment, and inclosed in a metal shield which is connected to one of its terminals, as shown in Figure 3. *C* is the condenser under test. It is inclosed in an earth-connected metal inclosure, and is connected to the bridge by means of leads which are also shielded, as shown in Figure 3. It will be observed that the oscillator *O* and detector *G* are connected to the bridge through two reversing switches *Z* and *Y* by means of shielded twin cable, and that the bridge is provided with a Wagner earth connection L_w P_w *E* R_w. This consists of a fixed resistor R_w of the same order as *R*,

[10] A. Campbell, Proc. Phys. Soc., vol. 20, p. 626, 1907.
[11] S. Butterworth, Proc. Phys. Soc., vol. 33, p. 313, 1921.
[12] D. W. Dye, Electrician, vol. 87, p. 55, 1921.

a variable resistor P_w, and a variable self inductor L_w. The point E is connected to earth, and by means of a small switch X, the telephone or galvanometer can be changed rapidly from position AB to AE.

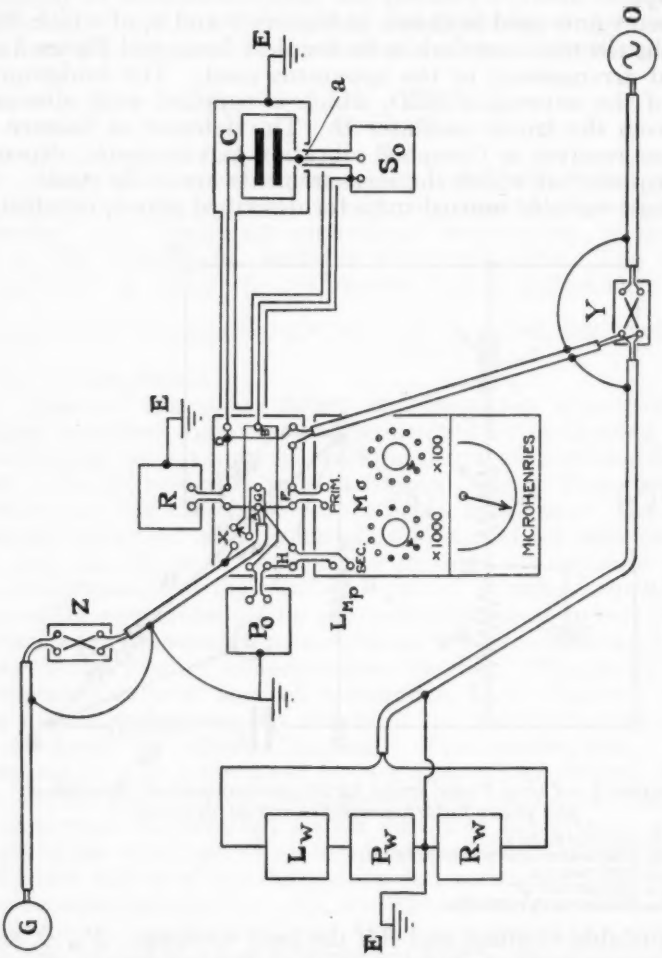

FIGURE 3.—*Carey Foster bridge*

The arrangement of the apparatus used at the National Physical Laboratory.

The equations of balance of the network $FABD$ are

$$C=\frac{M}{PR}\left[1+\frac{\omega^2 l_R(L-M)-l_s M\omega^2}{PR}+\frac{\sigma(R+S)}{PR}\right]$$

$$R+S_o+S_c=\frac{RL}{M}+P\frac{l_R}{M}+\frac{\sigma}{CM\omega^2}$$

where

C is the total capacitance of the arm DB, including the condenser and the residual capacitance of the shielded connecting leads.

S is the total effective resistance of the arm DB, including that of the resistor and connecting leads S_o and the effective series resistance of the condenser S_c.

$$S=S_o+S_c.$$

M and σ are the effective mutual inductance and impurity, respectively, between the arms FA and AB, in practice the values for the standard inductor.

L is the effective self-inductance of the arm AB, including the geometrical value of the fixed coil of the inductor L_o, the correction for capacitance and eddy current effects ΔL, and the self-inductance of the resistor and connecting leads l_p.

$$L = L_o + \Delta L + l_p$$

P is the effective resistance of the arm AB, including the value of the fixed resistor P_o, the d. c. resistance of the fixed coil of the inductor and the connecting leads, p, and the resistance correction for capacitance and eddy current effects in this coil Δp.

$$P = P_o + p + \Delta p$$

l_R and l_S are the residual self-inductance values of the resistors R and S_o, including the leads connecting them to the junction box of the bridge.

The equations may be thrown into more convenient practical forms by the substitution of the approximate relation $M = CPR$ in the small correcting terms. We then obtain for the value of C

$$C = \frac{M}{PR}\left[1 + (R+S)\,C\omega\delta_M + SC\omega\,(\delta_R - \delta_S)\right]$$

and for the loss angle δ of the condenser

$$\tan\delta = S_c C\omega = \left[\frac{RL}{M} - (R+S_o)\right] C\omega + \delta_R + \delta_M$$

where $\delta_R = \dfrac{l_R\omega}{R}$ and $\delta_S = \dfrac{l_S\omega}{S}$ are the phase angles of the resistors R and S respectively, and $\delta_M = \dfrac{\sigma}{M\omega}$ is the phase defect of the mutual inductor.

The main bridge is balanced by adjustments of M and S. The Wagner auxiliary balance is made by adjustments of L_w and P_w, and the various adjustments are made in succession until balance is obtained for both positions of the switch X. The effects of earth capacitance at the points A, B, D, and F are then eliminated from the readings of the bridge proper. It will be noticed that with the arrangement of screens used, the capacitance of the leads to the condenser are in this way eliminated from the measurements, as are also the earth capacitance of the shield of the condenser (or the outer plates, if it is unshielded), and the shield of the resistance box S_o. It should be noticed also that all external screens are brought to earth potential. The earth capacitance of the lead connecting S_o and C is not eliminated from the measurements and is apt to cause an error when small condensers are under test, unless this lead is kept as short as possible, and shielded as shown in Figure 3.

The readings of M and S corresponding to the condition of balance are noted. The reversing switches Y and Z are operated in turn, the bridge being rebalanced after each reversal. The mean of the four readings corresponding to the four possible relative positions

of these switches, is taken as the correct reading. The four readings differ by only a very slight amount, which represents the effect of stray inductances between oscillator, detector, and the various bridge components.

The temperatures of the coils P and R are noted so that their resistance values can be read from the calibration charts. The resistance (p) of the fixed coil of the inductor, and also that of the resistance S_o are then measured on a Wheatstone bridge with direct current.

The "zero" reading of the bridge is obtained as follows: The condenser is disconnected at the point (a) and the bridge again balanced. The reading of the inductor for this balance is very nearly zero; it represents the residual capacitance of the leads, terminals, etc., where the shielding is not quite perfect. In calculating the capacitance of the condenser from the above equation, this "leads" reading is subtracted from the value observed when the condenser is in circuit.

By a choice of suitable values for P and R, any capacitance in the range 10 μf to 0.01 μf, or even less, can be measured with accuracy on this bridge. Measurements on each condenser are usually made with two different sets of resistances, so as to get a check on each result, and the two values usually differ by less than 1 part in 10,000. Additional checks are obtained by measuring several condensers separately and then in parallel. The results given below provide examples of such measurements.

The values of P and R used for the majority of the measurements were:

C	P	R	M
μf	*Ohms*	*Ohms*	*mH*
1.0	200	50	10
	100	100	10
.5	200	100	10
	200	50	5
.2	500	100	10
	200	100	4
.1	500	200	10
	500	100	5
.05	1,000	200	10
	500	200	5
.02	1,000	500	10
	1,000	200	4
.01	2,000	500	10
	1,000	500	5

NOTE.—The value of S is, of course, determined by the values of R, L, and M.

VII. RESULTS

The results are embodied in Tables 1 to 6, inclusive. They naturally divide into two parts, namely, those on capacitance (Tables 1 to 4) and those on power factor (Tables 5 and 6).

In Table 1 are given the values of the capacitances as determined in 1928 at the two laboratories. The results indicate, as was shown by later measurements, that the capacitor during transportation from the United States to England on its first transit had been subjected to conditions that caused a decrease in the capacitance of each

of the sections. This rendered the intercomparison of little value. However, the differences as shown in Table 2 suggest that the measured value of the change of capacitance with frequency in the two laboratories was not the same by 1 or 2 parts in 10,000.

TABLE 1.—*Capacitance at four frequencies as measured in 1928*

[Capacitance in International Microfarads at 25.0±1° C.]

Condenser section	Bureau of Standards, May, 1928				National Physical Laboratory, November, 1928			
	60~	100~	1000~	2000~	60~	100~	1000~	2000~
0.01	0.010074	0.010073	0.010058	0.010059	0.010061	0.010055	0.010037	0.010033
.02	.020080	.020071	.020061	.020059	.020062	.020052	.020040	.020036
.02′	.020146	.020137	.020118	.020113	.020127	.020118	.020097	.020090
.05	.050076	.050059	.050019	.050013	.05004$_9$	.05003$_9$	.04998$_3$	.04996$_8$
.1	.10027	.10024	.10013	.10009	.10024	.10021	.10008	.10003
.1′	.10041	.10037	.10028	.10024	.10038	.10035	.10023	.10019
.2	.20005	.20002	.19991	.19983	.19997	.19993	.19980	.19972
.5	.50104	.50103	.50083	.50050	.5008$_6$	.5007$_8$	.5005$_1$	.5003$_5$
Σ1.0	1.0023	1.0022	1.0014	1.0012	1.0017	1.0016	1.0008	1.0002

TABLE 2.—*Differences in capacitance in parts in 10,000 between the Bureau of Standards results of May, 1928, and the National Physical Laboratory results of November, 1928*

[In all cases the Bureau of Standards results were larger]

Condenser section	60~	100~	1,000~	2,000~
0.01	13	18	21	26
.02	9	10	11	12
.02′	10	9	11	12
.05	5	6	7	10
.1	3	3	5	6
.1′	3	2	5	5
.2	4	5	6	6
.5	4	5	6	3
Σ1.0	6	6	6	10

A possible discrepancy of this order in the methods of measurement was considered to merit special attention, since the determination of this quantity is based on entirely different assumptions at the two laboratories. At the Bureau of Standards the capacitance of the air capacitor is assumed to be invariable with frequency. At the National Physical Laboratory the changes in the value of the standard mutual inductors are deduced from observations of self-capacitance made at radio-frequencies on specially constructed coils. In the subsequent measurements there was no consistent difference between the measured values of the change of capacitance with frequency, and it is concluded that both systems of measurement give the same result within the limits of error of this investigation.

The results, on individual sections, of all capacitance measurements subsequent to the first set made at the Bureau of Standards are given in Table 3. The values show a remarkably good agreement in the measurements at the two laboratories. When the work was begun the lack of stability of the capacitor (the best at that time available) was appreciated, and no effort made to obtain values

with an accuracy greater than 1 or 2 parts in 10,000. Hence, while the instability of the capacitor may explain the recorded differences, yet the possibility of an experimental error in the last recorded figure exists in every case. It appears certain that the microfarad and its subdivisions have the same value at the two laboratories as accurately as can be determined by transporting the present mica capacitor; that is, within 1 or 2 parts in 10,000. Since very different methods are used at the two laboratories for establishing the unit of capacitance from the units of resistance and time, this agreement shows that both methods give precise results. A more accurate comparison must await the construction of more stable standards.

TABLE 3.—*Values of capacitance of the individual sections of subdivided capacitor B. S. 16390 as determined at the National Physical Laboratory and the Bureau of Standards between January, 1929, and March, 1931, inclusive*

[Capacitance in microfarads]

	0.01 section		0.02 section	
	60~	1,000~	60~	1,000~
N. P. L., January, 1929	0.010061	0.010037	0.020062	0.020040
B. S., June, 1929	.010063	.010042	.020059	.020043
B. S., January, 1930	.010067	.010045	.020060	.020048
N. P. L., September, 1930	.010061	.010041	.020062	.020043
B. S., March, 1931	.010070	.010047	.020070	.020059
B. S., February, 1932	.010066	.010045	.020059	.020040
	0.02′ section		0.05 section	
	60~	1,000~	60~	1,000~
N. P. L., January, 1929	0.020127	0.020097	0.050049	0.049983
B. S., June, 1929	.020125	.020101	.050051	.049993
B. S., January, 1930	.020129	.020106	.050057	.050002
N. P. L., September, 1930	.020127	.020099	.050053	.050000
B. S., March, 1931	.020134	.020111	.050059	.050007
B. S., February, 1932	.020127	.020104	.050071	.050012
	0.1 section		0.1′ section	
	60~	1,000~	60~	1,000~
N. P. L., January, 1929	0.10024	0.10008	0.10038	0.10023
B. S., June, 1929	.10024	.10009	.10038	.10024
B. S., January, 1930	.10024	.10008	.10038	.10023
N. P. L., September, 1930	.10023	.10009	.10038	.10025
B. S., March, 1931	.10022	.10010	.10036	.10025
B. S., February, 1932	.10025	.10011	.10038	.10025
	0.2 section		0.5 section	
	60~	1,000~	60~	1,000~
N. P. L., January, 1929	0.19997	0.19980	0.50086	0.50051
B. S., June, 1929	.19999	.19983	.50095	.50060
B. S., January, 1930	.19999	.19983	.50091	.50061
N. P. L., September, 1930	.19998	.19984	.50083	.50050
B. S., March, 1931	.19996	.19985	.50081	.50063
B. S., February, 1932	.20000	.19981	.50093	.50070

The values obtained on the Σ sections are given in Table 4. The measured values were obtained by actual measurements on sections connected in parallel; the computed values are the sum of the measured values of the same sections as measured individually. The values are in exceptionally good agreement, the recorded differences being well within the limits of error of the measurements. The greatest difference is in the Bureau of Standards values of the Σ 0.05 section for March, 1931, where the measured and computed values differ by 4 parts in 10,000.

TABLE 4.—*Measured and computed values of capacitance of the Σ sections of subdivided capacitor B. S. 16390 as determined at the National Physical Laboratory and the Bureau of Standards between January, 1929, and March, 1931, inclusive*

[Capacitance in microfarads]

	Σ0.05 section			
	60~ measured	60~ computed	1,000~ measured	1,000~ computed
N. P. L., January, 1929	----------	0.050250	0.050181	0.050174
B. S., June, 1929	0.050248	.050247	.050193	.050186
B. S., January, 1930	.050256	.050256	.050198	.050200
N. P. L., September, 1930	----------	.050250	----------	.050183
B. S., March, 1931	.050253	.050274	----------	.050214
B. S., February, 1932	.050268	.050252	.50204	.050195
	Σ0.1 section			
N. P. L., January, 1929	----------	0.10030	0.10017	0.10016
B. S., June, 1929	0.10031	.10030	.10018	.10019
B. S., January, 1930	.10031	.10032	.10018	.10020
N. P. L., September, 1930	.10030	.10030	.10019	.10018
B. S., March, 1931	.10029	.10031	.10020	.10022
B. S., February, 1932	.10033	.10034	.10022	.10023
	Σ1.0 section			
N. P. L., January, 1929	1.0017	1.0018	1.0008	1.0008
B. S., June, 1929	1.0019	1.0019	1.0009	1.0009
B. S., January, 1930	1.0019	1.0018	1.0010	1.0010
N. P. L., September, 1930	1.0017	1.0017	1.0009	1.0009
B. S., March, 1931	1.0017	1.0016	1.0010	1.0010
B. S., February, 1932	1.0019	1.0019	1.0012	1.0011

The values of the power factor of the individual sections as obtained at 60 and 1,000 cycles are given in Table 5. As the power factor values are not affected by the capacitance changes which occurred during the first transit, the results of the first Bureau of Standards determination are inlcuded in the table. The values are in most cases given to the fifth decimal place (example: $16.1\times10^{-4}=0.00161$), since, for some sections, the differences between the two laboratories can only be made apparent by recording the fifth place. Variations in the fourth place are to be expected when the capacitance measurements are made with an accuracy of 1 in 10,000. There is no systematic difference between the values as obtained in the two laboratories. For all sections the agreement at 60 cycles is somewhat better than at 1,000 cycles. The differences in the tabulated values are probably the result of experimental errors.

The results of the measured and computed values of the power factor on the Σ sections are given in Table 6. The measured values

were obtained by a measurement on sections connected in parallel. The computed values were determined as the mean, weighted according to the value of the capacitance, of the measured values of the individual sections. The results are in substantial agreement for a given section at a given frequency. As with the individual section, the 60-cycle values show smaller differences than the 1,000-cycle values. The results for a given section can be depended upon to about one in the fourth decimal place.

TABLE 5.—*Values of power factor of the individual sections of subdivided capacitor B. S. 16390 as determined at the National Physical Laboratory and the Bureau of Standards between January, 1929, and March, 1931, inclusive*

[Values must be multiplied by 10^{-6}]

	0.01 section		0.02 section	
	60~	1,000~	60~	1,000~
B. S. April, 1928	16.1	11.0	8.2	3.2
N. P. L. January, 1929	15.	11.	6.	3.7
B. S. June, 1929	14.0	6.8	7.4	2.2
B. S. January, 1930	14.0	8.7	7.3	2.8
N. P. L. September, 1930	14.	9.2	7.5	2.5
B. S. March, 1931	14.9	7.0	7.4	2.5
B. S. February, 1932	14.8	10.3	7.8	2.7
	0.02′ section		0.05 section	
B. S. April, 1928	9.7	6.3	12.6	5.6
N. P. L. January, 1929	8.	6.6	11.	4.7
B. S. June, 1929	8.9	4.8	11.2	3.9
B. S. January, 1930	8.9	6.0	11.2	4.0
N. P. L. September, 1930	8.	5.0	11.2	4.4
B. S. March, 1931	9.5	4.9	10.1	3.0
B. S. February, 1932	9.4	5.6	11.3	4.8
	0.1 section		0.1′ section	
B. S. April, 1928	10.7	6.8	10.9	6.0
N. P. L. January, 1929	11.1	6.9	11.3	5.9
B. S. June, 1929	11.1	6.1	11.4	5.1
B. S. January, 1930	10.8	6.4	11.1	5.3
N. P. L. September, 1930	11.7	6.4	12.1	5.1
B. S. March, 1931	10.3	5.5	10.2	4.6
B. S. February, 1932	10.8	6.6	11.0	5.9
	0.2 section		0.5 section	
B. S. April, 1928	5.8	4.6	5.7	4.1
N. P. L. January, 1929	5.8	3.8	5.5	3.0
B. S. June, 1929	5.7	3.9	5.5	3.4
B. S. January, 1930	5.5	3.4	5.1	3.4
N. P. L. September, 1930	5.8	3.4	6.3	2.5
B. S. March, 1931	5.1	2.2	4.9	2.2
B. S. February, 1932	5.7	3.2	5.4	2.5

In addition to the data on power factor given in the tables, the power factor was determined at 100 and 2,000 cycles at the time of the first measurement in each laboratory. The agreement was about the same as for 60 and 1,000 cycles, so that tables giving these values do not appear.

TABLE 6.—*Measured and computed values of power factor of the Σ sections of subdivided capacitor B. S. 16390 as determined at the National Physical Laboratory and the Bureau of Standards between January, 1929, and March, 1931, inclusive*

[Values must be multiplied by 10^{-4}]

	Σ 0.05 section			
	60~ measured	60~ computed	1,000~ measured	1,000~ computed
B. S. April, 1928	10.3	10.4	5.6	5.8
N. P. L. January, 1929	----------	8.6	5.5	6.2
B. S. June, 1929	9.9	11.1	5.1	4.1
B. S. January, 1930	9.7	9.4	5.1	5.3
N. P. L. September, 1930	----------	9.0	----------	4.8
B. S. March, 1931	9.3	9.0	----------	4.4
B. S. February, 1932	9.7	10.3	5.5	5.4
	Σ 0.1 section			
B. S. April, 1928	11.1	11.6	5.6	5.8
N. P. L. January, 1929	----------	9.8	5.5	5.3
B. S. June, 1929	10.5	10.5	4.5	4.5
B. S. January, 1930	10.3	10.3	5.1	5.0
N. P. L. September, 1930	10.5	10.1	4.7	4.6
B. S. March, 1931	9.7	9.7	4.2	3.7
B. S. March, 1932	10.1	10.5	4.9	5.1
	Σ 1.0 section			
B. S. April, 1928	7.2	7.7	5.8	4.9
N. P. L. January, 1929	6.8	7.1	3.5	4.1
B. S. June, 1929	7.0	7.2	4.4	4.0
B. S. January, 1930	6.5	6.8	5.3	4.1
N. P. L. September, 1930	7.5	7.7	3.3	3.5
B. S. March, 1931	6.6	6.5	4.0	3.0
B. S. February, 1932	7.3	7.0	4.4	4.6

VIII. CONCLUSIONS

The following conclusions can be drawn from the information herein presented:

1. The transportation of a mica capacitor may cause a change in the capacitance even when there is no visible indication of damage.

2. So far as the measurements here reported are concerned, the capacitance of an air capacitor of the type used at the Bureau of Standards is independent of the method of measurement, at least with an accuracy of 1 part in 10,000.

3. The mutual inductance between the coils of the standard inductor of the National Physical Laboratory can be computed from its dimensions and a correction made for the capacitance between the coils for all frequencies here reported, at least with an accuracy of 1 part in 10,000.

4. The unit of capacitance, the microfarad, is the same in the Bureau of Standards and the National Physical Laboratory within the limits of accuracy of the present measurements, about 1 in 10,000.

5. Measurements at the two laboratories of the power factor at any frequency below 1,000 cycles give values which agree to one or two in the fourth decimal place.

6. Increased accuracy in intercomparison must await the development of more stable standards of capacitance.

The authors wish to express appreciation of the help received from their associates in the two laboratories.

WASHINGTON and TEDDINGTON, March 1, 1932.

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ISOLATION AND DETERMINATION OF NORMAL HEPTANE AND OF METHYLCYCLOHEXANE IN A MIDCONTINENT PETROLEUM

(INCLUDING A DETERMINATION OF THE PHASE EQUILIBRIUM DIAGRAM FOR THE CONDENSED SYSTEM NORMAL HEPTANE-METHYLCYCLOHEXANE)[1] [2]

By Mildred M. Hicks-Bruun and Johannes H. Bruun [3]

ABSTRACT

An Oklahoma petroleum was fractionated by distillation into a series of 1° cuts. After removal of the toluene from the fractions boiling between 93° to 101°C., by nitration, and subsequent fractional distillations, most of the heptane and the methylcyclohexane were found to concentrate in the fractions boiling between 98° and 100°C. Both of these hydrocarbons were isolated in a practically pure condition by further distillation through a 35-foot laboratory column. For the final fractionation of the material by equilibrium melting a specially designed freezing apparatus and a centrifuge adapted for low-temperature work were used.

The following physical constants were determined for the isolated *n*-heptane and methylcyclohexane: Specific gravity, refractive index, boiling point, freezing point, aniline point, and molecular weight. Photographs were also taken of the infra-red absorption spectrum of the isolated hydrocarbon. The purity of both compounds was calculated to be above 99.8 mole per cent. Based upon the crude petroleum, it was found that not less than 0.9 per cent of *n*-heptane and not less than 0.3 per cent of methylcyclohexane are present.

It was found that, contrary to a statement in the literature, a constant boiling mixture of *n*-heptane and methylcyclohexane is not formed and hence that a complete separation of the mixture is possible by distillation alone.

The phase-equilibrium diagram for the condensed system *n*-heptane-methylcyclohexane was determined and the eutectic mixture corresponding to about 93 weight per cent of methylcyclohexane was found to freeze at −130.3° C.

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[1] Presented before the division of petroleum chemistry at the meeting of the American Chemical Society, New Orleans, La., Mar. 30, 1932.

[2] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

[3] Research associate for the American Petroleum Institute.

I. HISTORICAL

1. *n*-HEPTANE

Although the presence of *n*-heptane in petroleum has been indicated by Schorlemmer (1),[4] Beilstein and Kurbatoff (2), Charitschkow (3), and others (4) during the earliest stages of petroleum research, the isolation of this hydrocarbon in a pure state from petroleum has been attended with many difficulties. Many investigators (4) have reported the isolation of *n*-heptane from petroleum, but the physical constants of their samples, when given, indicate that in practically every case the material regarded as "heptane" consisted of a mixture of heptane with considerable quantities of naphthene hydrocarbons.

As examples, we may take the heptane samples reported by Warren (5) and by Mabery (6). These samples had boiling points which were nearly the same as that of pure *n*-heptane, but combustion analyses indicated that the carbon-hydrogen ratio was too large to correspond to a pure paraffin hydrocarbon. From this fact as well as from the values which these investigators reported for the vapor density, it is apparent that their samples of "*n*-heptane" were contaminated with considerable quantities of naphthene hydrocarbons.

In more recent years Anderson and Erskine (7) and Brown and Carr (8) have made further attempts to isolate *n*-heptane from petroleum by distillation alone. However, the specific gravity ($d_{15.5}^{15.5}=0.7117$ instead of 0.6867) given by the former and the refractive index ($n_D^{20}=1.4068$ instead of 1.3877) given by the latter investigators indicate that their samples also were mixtures of *n*-heptane with naphthenes and possibly with other hydrocarbons. Francis and Young (9) subjected their heptane fractions to treatments with bromine. The resulting monobromides were then fractionated by distillation at reduced pressures after which the *n*-heptyl bromide fraction was reduced to *n*-heptane. In this way a small sample of nearly pure heptane was obtained.

The most recent publication on the isolation of *n*-heptane from petroleum is that of Shepard, Henne, and Midgley (10). These investigators used a combination of distillation and a vigorous treatment with chlorosulphonic acid (11), and were able to isolate the *n*-heptane in an extremely pure condition. While the chlorosulphonic acid method gives a rapid means of obtaining normal paraffin hydrocarbons from petroleum, it could not be employed in the present instance since this reagent not only partially destroys the *n*-heptane, but also completely destroys the branch chain and cyclic hydrocarbons and thus renders impossible their identification and determination in the petroleum.

2. METHYLCYCLOHEXANE

Methylcyclohexane has apparently never been isolated from petroleum in a demonstrably pure condition. However, its presence in different crude petroleums has been indicated by investigators, such as Lachowicz (12), Charitschkow (13), Young (14), Poni (15), Mabery and Sieplein (16), and Markownikoff (17).

[4] Numbers in parentheses here and elsewhere in the text refer to the bibliography at the end of the paper.

II. METHODS EMPLOYED AND APPARATUS USED

The petroleum fractions used for this investigation were distilled by S. T. Schicktanz and a staff of assistants in rectifying stills of Pyrex laboratory glass. A complete description of the distillation equipment as well as methods of operating the stills has been published in a recent paper (18).

After the preliminary distillations, the toluene was removed from the fractions, boiling between 93° and 101° C., by means of a nitrating

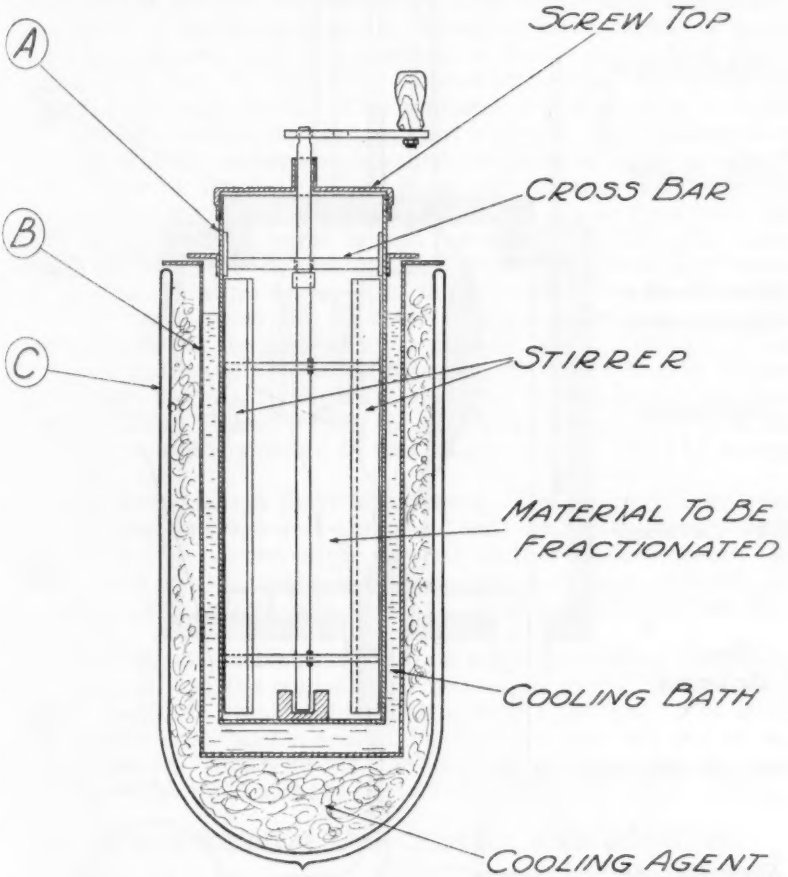

FIGURE 1.—*Apparatus for freezing the material to be fractionated by equilibrium melting*

treatment previously described (19). After the final distillations, further purification of the heptane as well as of the methylcyclohexane was accomplished by equilibrium melting. For this purpose the material was cooled in a freezing apparatus until a large amount of the solid phase had crystallized out. In this way the impurities were concentrated in the "mother liquor" which was separated subsequently from the pure solid crystals by means of a centrifuge suitable for low temperature work.

The freezing apparatus is shown in Figure 1.[5] The material to be fractionated was introduced into the brass freezing vessel, *A*, which was provided with a top to prevent condensation of moisture from the air and a stirrer. The freezing vessel, *A*, was placed in a brass cooling

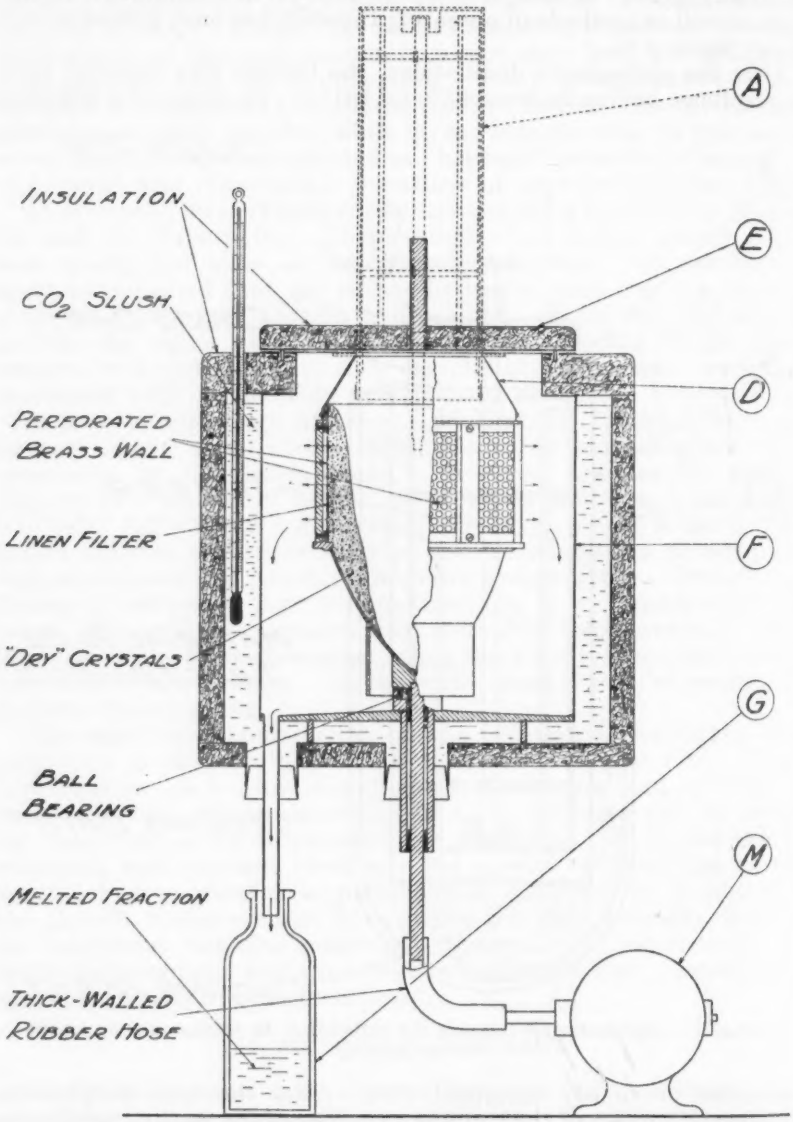

FIGURE 2.—*Centrifuge for fractionation by equilibrium melting*

bath, *B*, which was filled with a suitable liquid.[6] The two brass vessels, *A* and *B*, were then placed in a Pyrex Dewar flask, *C*, and cooled. The preliminary cooling, to about −80° C., was accom-

[5] Acknowledgment is made to F. W. Rose for drawing all of the figures in this paper.

[6] For information concerning noninflammable liquid mixtures having low freezing points the reader is referred to a paper by Kanolt (20).

plished by means of a slush of solid carbon dioxide, carbon tetrachloride and chloroform. Further cooling of the petroleum fraction to its freezing point, and finally to solidification, was accomplished by means of liquid air or liquid nitrogen. In order to prevent the material in the vessel, *A*, from freezing to a hard mass, it was necessary to provide constant agitation during freezing. For the same reason, it was desirable to maintain the temperature of the cooling bath only a few degrees below the freezing point of the material to be fractionated. In this way a soft crystalline slush can be obtained easily for materials which contain comparatively large amounts of impurities.

Compounds of fairly high purity, however, have usually a great tendency to supercool and then suddenly to freeze into a hard mass. Because of this fact, the following method of freezing was preferred for nearly pure compounds. The material was placed in a brass cylinder provided with a top (but without a stirrer), then precooled to about −80° C. with carbon dioxide slush, and finally frozen to a hard mass by means of liquid air. The brass cylinder was then removed from the cooling agent and allowed to stand in a Dewar flask until the hard crystalline material began to melt into a soft, but still solid mass.

As soon as this had been accomplished the material was transferred rapidly into the rotating drum, *D*, of the centrifuge (see fig. 2) which had already been cooled to −80° C.[7] This transfer was made by momentarily placing the freezing apparatus, *A*, in an inverted position on the top of the centrifuge, as indicated by the dotted lines in Figure 2. The frozen material in the rotating drum, *D*, was broken up, and stirred to a uniform mass. Then the centrifuge was covered with the top, *E*, and the rotating drum, *D*, was set into rapid motion by means of the motor, *M*.

The cylindrical walls in the rotating drum, *D*, in the centrifuge were made of perforated brass and were lined with fine linen cloth. This allowed the melted portion of the crystals, or the "mother liquor," to be thrown out by the rotating motion into the brass cylinder, *F*. From here it passed down into the flask, *G*, and constituted the first "fraction."

The "dry" crystals which remained on the inside wall of the drum, *D* were scraped into the cone-shaped bottom of vessel, *D*, and were allowed to melt into a slush under intermittent agitation. The drum *D*, was rotated again and a second fraction was run off, and so on. The last fraction consisting of the highest melting crystals was removed from the walls and the bottom of *D* with the aid of a spoon.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. PRELIMINARY DISTILLATION OF THE CRUDE PETROLEUM AND SUBSEQUENT REMOVAL OF THE TOLUENE

The crude petroleum used for this investigation was obtained from No. 6 well of the South Ponca Field, Kay County, Okla. The properties as well as the preliminary distillations of the crude oil have been described in previous papers (21) (22). The amounts of material obtained in separate 1° C. cuts are shown in Figure 3. The largest

[7] The centrifuge shown in Figure 2 is designed primarily for fractionation of compounds having freezing points above −80° C. For mixtures with lower initial freezing points a more efficient separation could be obtained if a liquid air-cooled jacket were placed between the rotating drum *D* and the wall of the brass cylinder *F*. Thus a slower melting of the material placed in the rotating drum *D* could be accomplished and consequently it would be easier to obtain equilibrium conditions between the solid and liquid phases.

amount is shown to have distilled between 98° and 99° C. or around the boiling point of *n*-heptane. After the preliminary distillations, all of the fractions were subjected to a nitrating treatment for the purpose of removing and determining the toluene. The isolation of toluene from these fractions has been described in a previous publication. (19.) After the nitrating treatment the fractions were

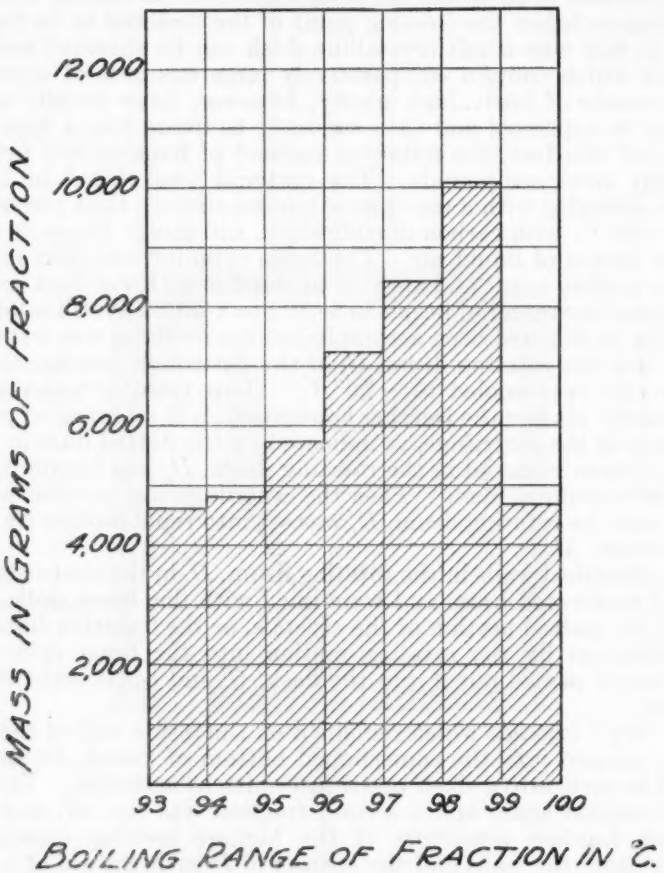

FIGURE 3.—*Distribution of the fractions over their boiling range before removal of the toluene*

washed with a solution of sodium hydroxide and with distilled water and finally dried over calcium chloride.

2. FURTHER FRACTIONATION OF THE MATERIAL AND PRELIMINARY IDENTIFICATION OF *n*-HEPTANE AND METHYLCYCLOHEXANE

The toluene-free fractions were subjected to further distillations in 30-plate rectifying stills of glass. (18.) Most of the material with boiling points between 93° and 97° was concentrated into two large fractions boiling around 92° C. and around 98° C., respectively. As shown in Figure 4 about 12,500 g of material distilled near the boiling point of *n*-heptane (98° and 99° C.). The initial freezing points and

the refractive indices of the fractions were determined and plotted against their boiling ranges. (See fig. 5.)

From the physical constants of the fractions it was apparent that the mixtures consisted of *n*-heptane and methylcyclohexane. This was confirmed in the following way:

1. A 1,000 g sample of the 98° to 99° cut was agitated with chlorosulphonic acid at 40° C. for eight hours. The acid layer was then replaced with fresh acid after which the mixture was agitated at 40° C.

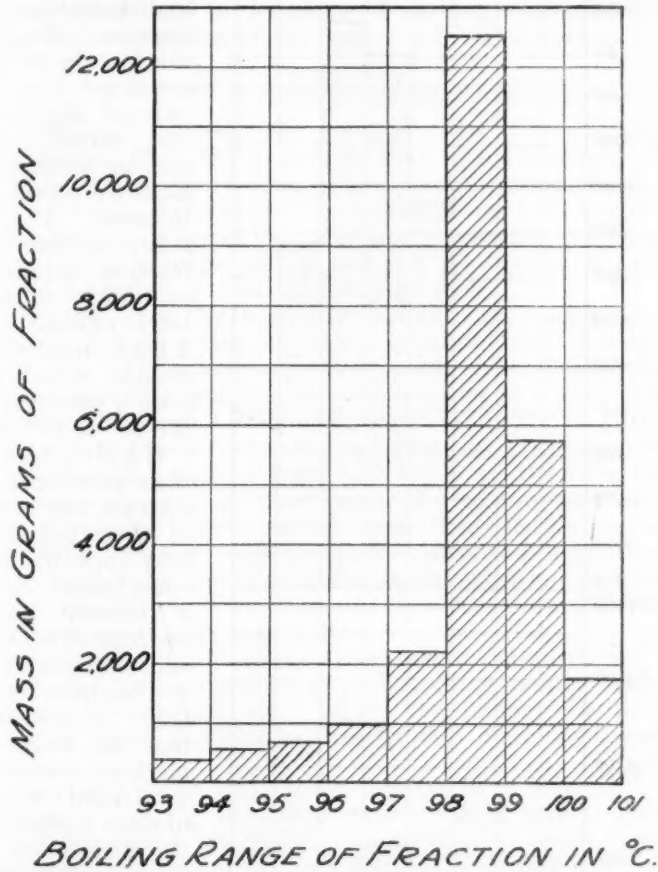

FIGURE 4.—*Distribution of the fractions over their boiling range after removal of the toluene and subsequent fractional distillation*

for another eight hours. The remaining unattacked hydrocarbon layer was finally washed with sodium hydroxide solution and with water after which it was distilled over sodium hydroxide in a 10-plate bubbling-cap still. The middle portion of the distillates was found to consist of nearly pure *n*-heptane as indicated by its freezing (−90.68° C.), its narrow freezing range and its other physical constants.

2. Another sample of the 98° to 99° cut was passed through a dehydrogenation furnace filled with palladinized asbestos and maintained at about 350° C. The reaction products, which had a distinct odor of toluene, were then subjected to nitration at 5° C., as a result of which a yellow nitroproduct was obtained. This nitroproduct was identified as, 2, 4-dinitrotoluene, which confirmed the formation of toluene by dehydrogenation of the fraction. Because of this fact the 98° to 99° cut must have contained dihydrotoluene, tetrahydrotoluene, or methylcyclohexane (hexahydrotoluene). The zero iodine number of the fraction excluded the possibility of di- or tetrahydrotoluene. Thus methylcyclohexane must have been a constituent of the 98° to 99° cut.

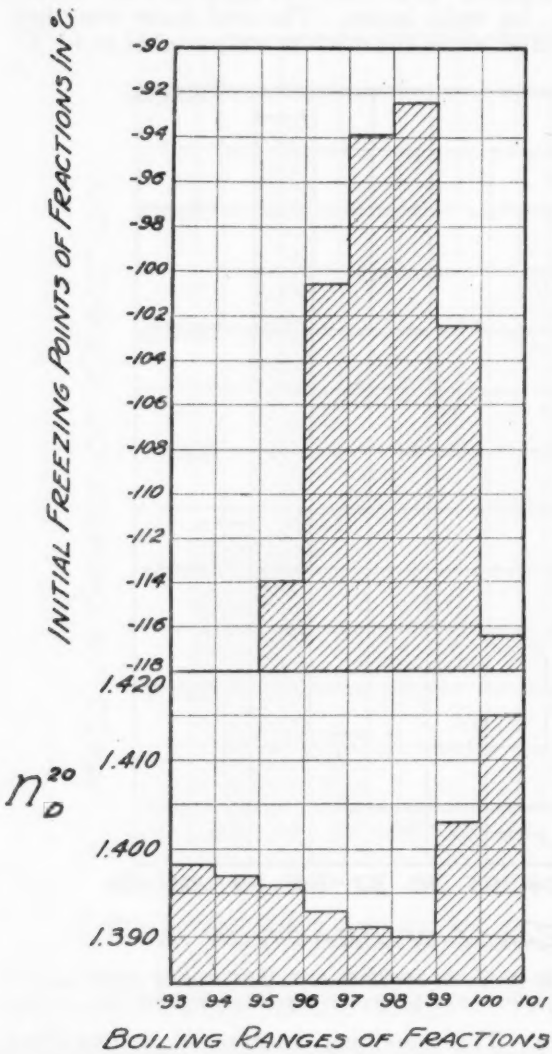

FIGURE 5.—*The initial freezing points and the refractive indices of the fractions plotted against their boiling ranges*

Having identified the constituents of the mixture the problem of their isolation at first appeared rather complicated because a constant boiling mixture of *n*-heptane and methylcyclohexane has been reported (23). In view of this fact the following methods of separation were tried: (*a*) Equilibrium melting (21), (*b*) distillation with alcohols (24), (*c*) extraction with aniline (25), and (*d*) extraction with SO_2 (26). While none of these methods alone would give a sharp separation it was found that a combination of equilibrium melting and of distillation with methyl or ethyl alcohol gave a fairly good separation. Thus it was possible to obtain a small sample of methylcyclohexane, the freezing point and other physical constants of which indicated a purity of above 98 mole per cent.

Separation of larger quantities of methylcyclohexane by this method was abandoned because at this point it was discovered that the reported constant-boiling minimum with *n*-heptane does not exist. This was confirmed in the following way: A sample of pure synthetic *n*-heptane was kept continuously boiling in a boiling-point apparatus of the Cottrell (27) type. As soon as a constant temperature reading was observed, small quantities of pure synthetic methylcyclohexane were introduced into the boiling-point apparatus through the condenser and the thermometer readings were recorded. The boiling point was determined for solutions of varying concentrations, but in no case could a lowering of the boiling point be observed.

3. Isolation of *n*-Heptane and Methylcyclohexane

The difference between the boiling points of methylcyclohexane and *n*-heptane (2.4° C.) is greater than the differences (0.35° and 1.05° C.) between the boiling points of the corresponding constant boiling mixtures of the respective hydrocarbons with methyl or ethyl alcohol (28). Consequently, a greater separation of these hydrocarbons should be expected by ordinary distillation than by distillation after admixture with the lower alcohols.

Accordingly, the fractions containing the *n*-heptane and the methylcyclohexane were subjected to careful distillations in a 35-foot column (18) packed with jack chain. These distillations were made at a rate of about 1 ml per minute and at a 10:1 reflux ratio. Five charges of about 2 liters each of the 98° to 99° C. cuts were put into the still and each charge was separated by distillation into about 30 fractions. For each of these 150 fractions, the refractive index, the boiling point, and, in most cases, the freezing point were determined. The lower boiling fractions from these distillations which had substantially the same refractive indices as pure *n*-heptane and freezing points not more than 0.5° below the freezing point of this hydrocarbon, were mixed. Two liters of this mixture were redistilled and yielded practically pure *n*-heptane.

The higher-boiling fractions from the above-mentioned five distillations had refractive indices and freezing points near those of methylcyclohexane and were mixed for further distillation. As a result of these distillations nearly pure methylcyclohexane was obtained.

In order to remove some of the last traces of impurities from the *n*-heptane, a 1,000 g sample of this material was subjected to a chlorosulphonic-acid treatment. As a result of this treatment and a subsequent distillation through a 30-plate column, heptane with a freezing point of -90.6_2 ° C. was obtained.

Another sample of the heptane material (with a boiling point 98.4° and a refractive index $n_D^{20}=1.3878$) as well as some of the best fractions of the methylcyclohexane were subjected to further purification by equilibrium melting with the aid of the centrifuge. As an illustration of the separations which were obtained with the aid of the centrifuge, the results of two different fractionations of *n*-heptane are shown in Table 1. Some additional physical constants of the fraction with freezing point −90.66 are given in Table 2.

TABLE 1.—*Some of the results obtained by submitting n-heptane samples of different degrees of purity to fractionations by centrifuging the crystals*

	Volume	Freezing point	Purity
	ml	*°C.*	*Mole per cent*
Fractionation of *n*-heptane of low purity:			
Original material	500	−93.99	83.9
First fraction	107	−95.59	77.1
Second fraction	144	−95.44	77.7
Third fraction	113	−93.81	84.7
Fourth fraction	49	−92.21	92.2
Fifth fraction	73	−90.91	98.5
Fractionation of *n*-heptane of fairly high purity:			
Original material	225	−90.96	98.3
First fraction	50	−91.17	97.2
Second fraction	40	−90.99	98.2
Third fraction	70	−90.91	98.5
Fourth fraction	50	−90.66	99.8

4. DETERMINATION OF THE FREEZING POINT-COMPOSITION DIAGRAM OF THE BINARY SYSTEM: *n*-HEPTANE-METHYLCYCLOHEXANE

In order to be able to determine the approximate composition of the fractions shown in Figure 4, the freezing point-composition diagram for the system: *n*-heptane-methylcyclohexane was determined. For this purpose synthetic mixtures of known composition of *n*-heptane and methylcyclohexane were made up.[8] The refractive index and the initial freezing point of each mixture were determined. The results are shown in Figure 6. It will be noted that the eutectic mixture of *n*-heptane and methylcyclohexane corresponds to about 93 weight per cent of methylcyclohexane and freezes at about −130.3° C.

IV. DISCUSSION OF THE RESULTS

In Table 2 a comparison is given between the physical constants of the best samples of *n*-heptane obtained in this work and the constants of *n*-heptane determined by other investigators.

TABLE 2.—*Physical constants of n-heptane*

n-heptane C_7H_{16}	d_4^{20}	n_D^{20}	Boiling point (corrected)	Freezing point (in dry air)	Critical solution temperature in aniline	Molecular weight
			°C.	*°C.*	*°C.*	
Hicks-Bruun and Bruun:						
1. Obtained by distillation	[a] 0.68437	[b] 1.3877	98.4	−90.81	[d] 70.0	[e] 100.1
2. Obtained by chlorosulphonic acid treatment	[a] .68365	[b] 1.3877	98.4	[c] −90.62	[d] 70.0	[e] 100.1
3. Obtained by centrifuging the crystals	[a] .68376	[b] 1.3877	98.4	[c] −90.66	[d] 70.0	[e] 100.1 (theoretical 100.12)
Shepard, Henne, and Midgley (10)	.68378	1.38775	98.38	−90.65	69.9	----------
Edgar and Calingaert (29)	.6836	1.38777	98.4	−90.5	70.0	----------

[a] Determined by the section of capacity and density of this bureau.
[b] Determined by L. W. Tilton, of the optical division of this bureau.
[c] The value for the freezing point of this sample was checked by B. J. Mair by means of a platinum resistance thermometer.
[d] The weight percentage of *n*-heptane in the mixture giving its critical solution temperature with aniline was found to be approximately 45. Shepard, Henne, and Midgley (11) report about 66 weight per cent.
[e] For method see M. M. Hicks-Bruun, B. S. Jour. Research, vol. 5, p. 575, 1930.

[8] The methylcyclohexane was obtained from the Bureau International des Etalons Physico-Chimiques and the *n*-heptane from the Ethyl Gasoline Corporation. The source of the latter was Jeffrey's pine.

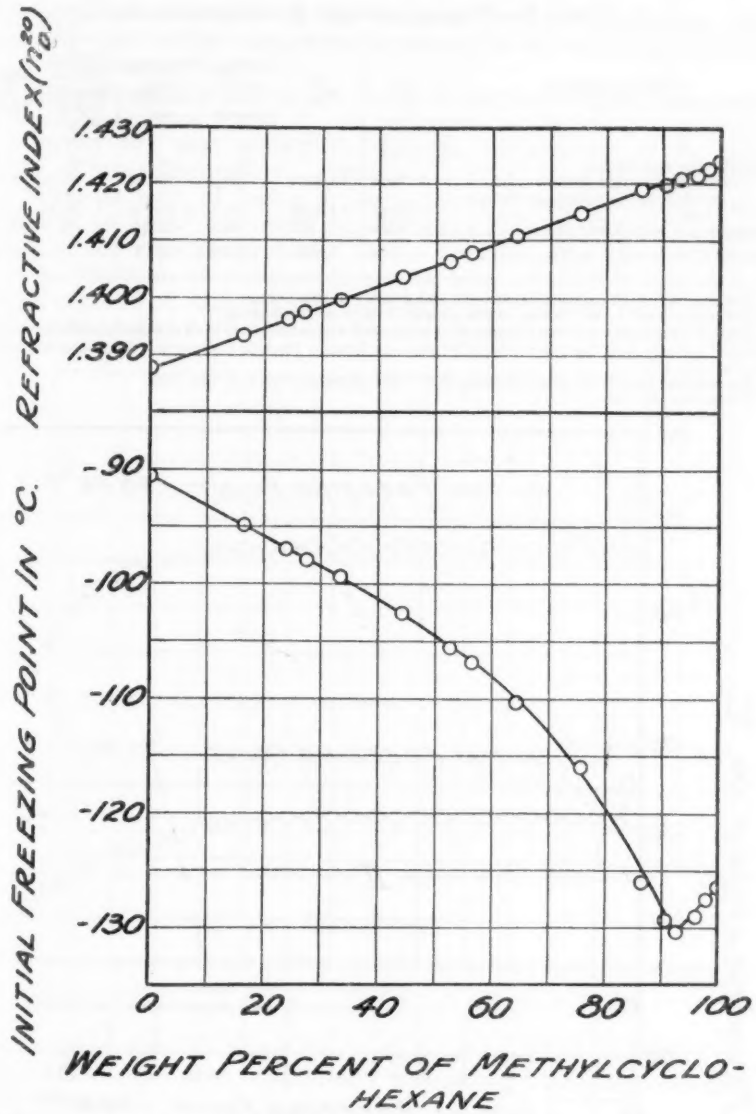

FIGURE 6.—*The phase equilibrium diagram for the condensed system n-heptane-methylcyclohexane*

The upper curve shows the refractive index $\left(n_D^{20}\right)$ plotted against the composition of the synthetic mixture In the lower graph the freezing point of the mixture is plotted against the composition.

TABLE 3.—*Physical constants of methylcyclohexane*

Methylcyclohexane C_7H_{14}	d_4^{20}	n_D^{20}	Boiling point (corrected)	Freezing point (in dry air)	Critical solution temperature in aniline	Molecular weight [4]
Hicks-Bruun and Bruun:			°C.	°C.	°C.	
1. Obtained by distillation	[1] 0.76918	[2] 1.4234	100.8	[3] −126.53	41.0	−[4] 98.1
2. Purified by centrifuging the crystals	[1] .76925	[2] 1.4234	100.8	[3] −126.44	41.0	−[4] 98.1
Timmermans and Martin (30)	.76929	1.423	101.2	−126.4	41	
Int. Crit. Tables, vol. 1, p. 214	.764	1.4235	100.8	−126.4		

[1] Determined by the section of capacity and density of this bureau.
[2] Determined by L. W. Tilton, of the optical division of this bureau.
[3] The freezing points on these samples were compared with a sample of pure synthetic methylcyclohexane obtained directly from the International Bureau des Étalons Physico-Chimique. The latter was found to freeze at −126.40°C.
[4] For method see M. M. Hicks-Bruun, B. S. Jour. Research vol. 5, p. 575, 1930.
[5] Theoretical 98.108.

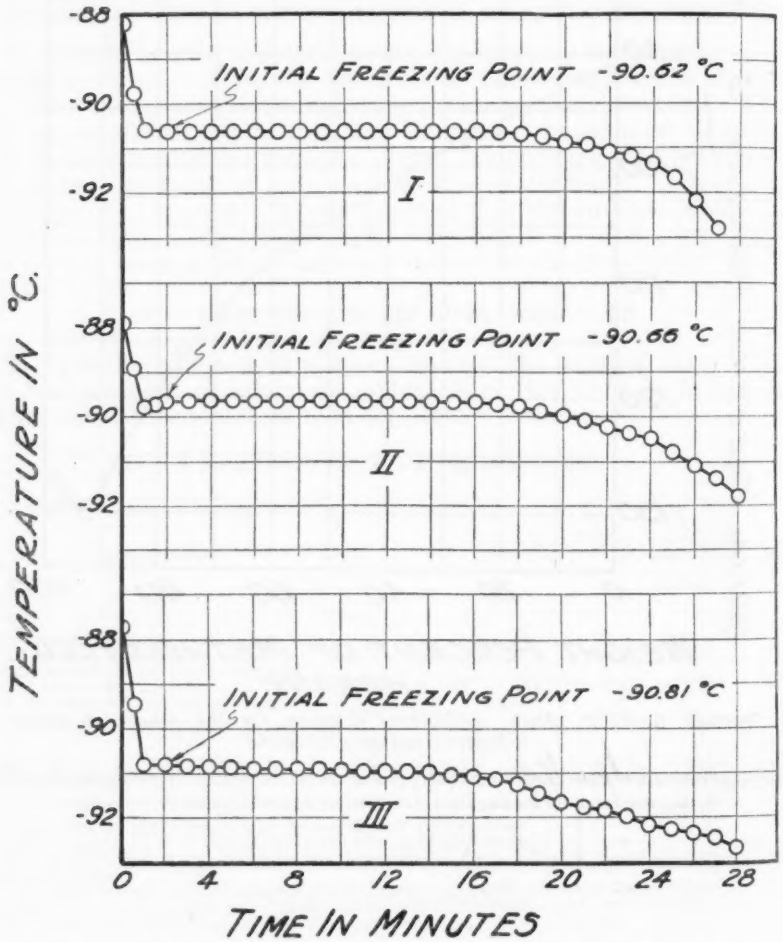

FIGURE 7.—*Time-temperature cooling curve for the isolated n-heptane*

Curve I refers to *n*-heptane obtained by treatment with chlorosulphonic acid. Curve II refers to *n*-heptane purified by equilibrium melting and centrifuging. Curve III refers to *n*-heptane obtained by distillation.

The physical constants of the isolated methylcyclohexane, together with some of the most reliable values for the synthetic hydrocarbon, are given in Table 3.

The time-temperature freezing curves of the isolated hydrocarbons are shown in Figures 7 and 8. In reference to Figure 8 it may be well to point out that methylcyclohexane, on account of its high viscosity at low temperatures, exhibits a marked tendency to supercool. Since its heat of fusion is comparatively small, caution must be observed to avoid too much supercooling, in order that the temperature of the crystals may rise to the true freezing point. However, crystallization of the sample can be effected readily, either by the usual method of adding a few solid crystals when the temperature of the liquid is slightly below the freezing point, or by first freezing

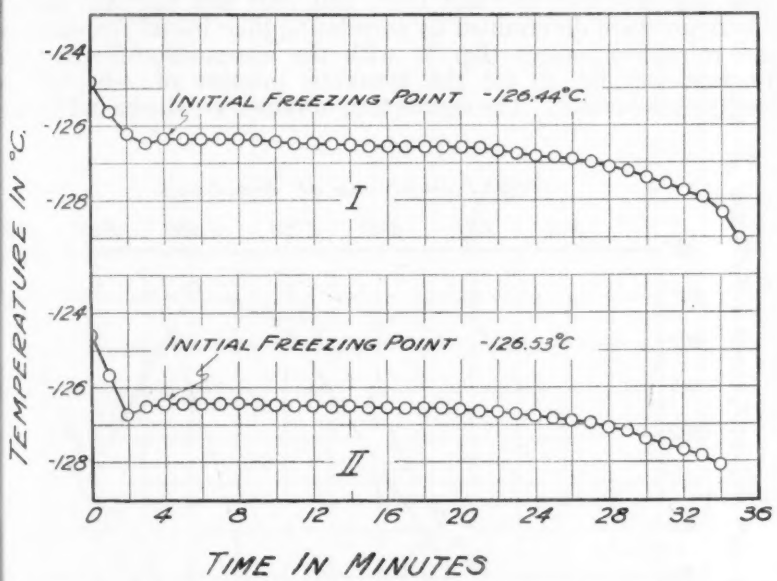

FIGURE 8.—*Time-temperature cooling curve for the isolated methylcyclohexane*

Curve I refers to methylcyclohexane purified by equilibrium melting and centrifuging. Curve II refers to methycyclohexane obtained by distillation.

the fraction and then allowing it to melt slowly until almost all of the crystals have disappeared, and finally proceeding with the cooling in the usual manner.

The infra-red absorption spectra of the isolated hydrocarbons are shown in Figures 9 and 10. These were determined by U. Liddel, of the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture.

The purity of the best samples of *n*-heptane and methylcyclohexane isolated was calculated from their freezing points and the known values (31) of their heats of fusion (33.7 and 16.2 calories per gram, respectively). The results of these calculations are shown in Table 4.

TABLE 4

	Calculated purity
	Mole per cent
n-heptane purified by centrifuging the crystals	99.8
n-heptane purified by chlorosulphonic acid treatment	100.0
n-heptane isolated by distillation	99.0
Methylcyclohexane purified by centrifuging the crystals	99.8
Methylcyclohexane isolated by distillation	99.5

In order to compute the approximate quantities of *n*-heptane and methylcyclohexane which are present in the crude petroleum the reader is referred to Figure 4. The compositions of three large fractions (98° and 99°, 99° and 100°, and 100° and 101° C.) shown in this figure were determined by correlating their initial freezing points and refractive indices (fig. 5) with the composition-freezing point diagram (see fig. 6) for the synthetic mixture of *n*-heptane and methylcyclohexane. The results thus obtained are shown in Figure 11.

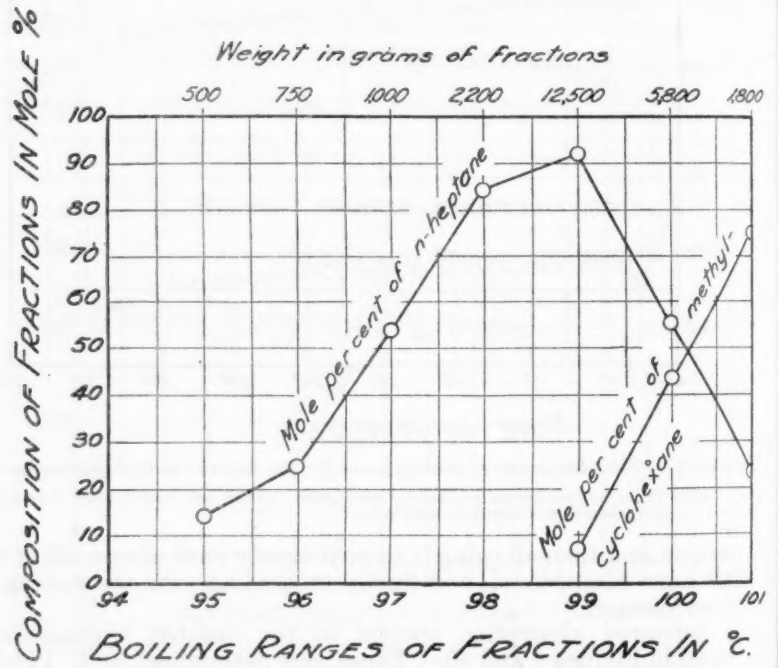

FIGURE 11.—*Composition of the fractions shown in Figure 4*

The mole percentage is plotted against the end temperature of each cut. The numbers at the top of the diagram show the weight in grams of each cut represented below

The fractions boiling between 95° and 98° C. were not binary mixtures, but contained lower boiling naphthenes and isomers of heptane. The mole per cent of *n*-heptane contained in these fractions has been calculated from their initial freezing points.

It was estimated from the results of further distillation that these fractions and the smaller fractions boiling between 93° and 95° contained about 2,700 g of *n*-heptane and 100 g of methylcyclohexane.

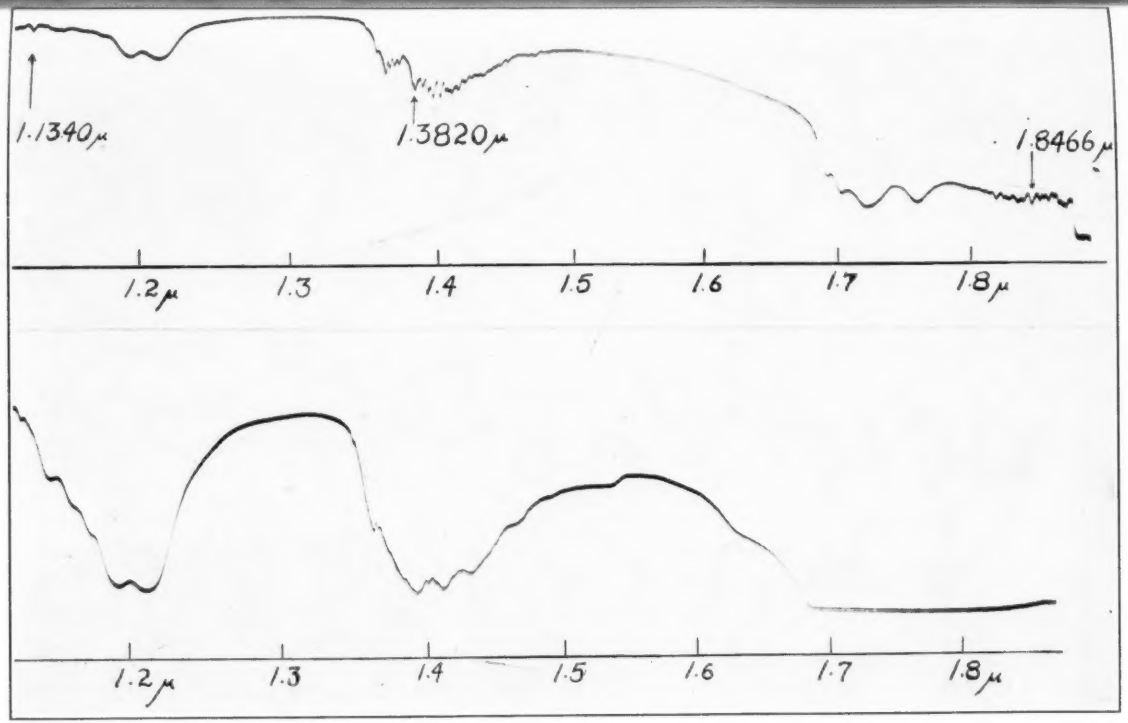

FIGURE 9.—*The infra-red absorption spectrum of the isolated n-heptane*

These curves are the energy transmission lines of the emission of a tungsten filament lamp through 1 mm and 1 cm cell thicknesses, respectively, of normal heptane, automatically recorded by an infra-red spectrograph in the region from 1 to 2 μ. These curves show the absorption of the compound at the first and second overtone frequencies of the 3.4 μ fundamental of hydrocarbon absorption at 1.73 μ and 1.20 μ and the combination band of this fundamental with another near 6 μ at 1.42 μ, besides the absorption of the water vapor necessarily present in the light path which is quite apparent as the fine band absorption and strong bands of which are indicated by the arrows. These spectra fit in nicely with the series of normal aliphatic hydrocarbon spectra studied by F. S. Brackett (Proc. National Acad. Sci., vol. 14, p. 861 (1928)). The records were taken with an effective slit width of approximate 20 A. Measured by U. Liddel, of the Fixed Nitrogen Research Laboratory, United States Department of Agriculture.

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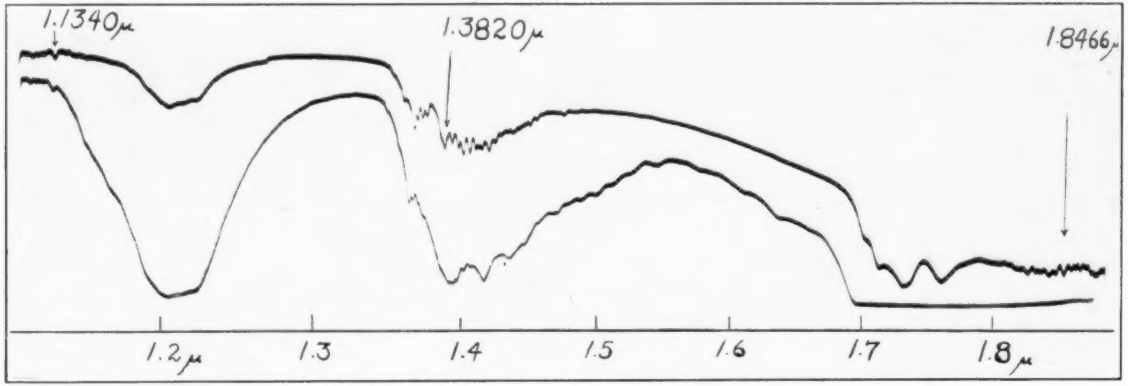

FIGURE 10.—*The infra-red absorption spectrum of the isolated methylcyclohexane*

The upper and the lower curves represent the transmission lines of the emission of a tungsten filament lamp through 1 mm and 1 cm cell thicknesses, respectively, of methylcyclohexane automatically recorded by an infra-red spectrograph in the region from 1 to 2 μ. These curves show the absorption of the compound at the first and second overtone frequencies of the 3.4 μ fundamental of hydrocarbon absorption at 1.74 μ and 1.21 μ and the combination band of this fundamental with another near 6 μ at 1.42 μ, besides the absorption of the water vapor necessarily present in the light path which is quite apparent as the fine band absorption and strong bands of which are indicated by the arrows. The records were taken with an effective slit width of approximately 20 A. Measured by U. Liddel, of the Fixed Nitrogen Research Laboratory, United States Department of Agriculture.

The other constituents of these fractions have boiling points of about 92° C. and are being further investigated. It should be noted that it was impossible to obtain the freezing points for the fractions with boiling ranges below 94.5° C. as these form glasses when cooled to low temperatures. This phenomenon has been found previously to be associated with the fact that isoparaffins and isonaphthenes, even when present in small quantities, often tend to cause abnormal supercooling or to prevent the crystallization of a mixture altogether.

It was concluded that the following values are a conservative estimate of the quantities of the hydrocarbons in the fractions shown in Figure 3:

	g
n-heptane	17,800
methylcyclohexane	[1] 6,000

Based upon the crude petroleum (600 gallons, specific gravity 0.9) it is estimated that not less than 0.9 per cent of *n*-heptane and not less than 0.3 per cent of methylcyclohexane is present.

From a motor fuel standpoint it is well known that *n*-heptane, because of its poor detonation characteristics, is an undesirable constituent of the gasoline fraction. Consequently, the antiknock properties of this fraction could be improved if most of the *n*-heptane were removed by fractional distillation. This procedure could be applied to those petroleums of which the 98° and 99° C. cut consists mainly of *n*-heptane. A partial utilization of the heptane fraction could probably be found, if it were first purified by subjecting it to about two treatments with chlorosulphonic acid and a subsequent fractional distillation. In this way *n*-heptane of sufficiently high purity for antiknock standards could be obtained. The manufacturing cost of the *n*-heptane would probably be low enough to permit the use of this hydrocarbon as a constituent not only of the present-day antiknock standards, but also of the more widely used secondary standards.

V. ACKNOWLEDGMENT

The authors acknowledge the technical advice of E. W. Washburn, director of American Petroleum Institute project No. 6.

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WASHINGTON, January 12, 1932.

RP 433

THE SPECTRAL ERYTHEMIC REACTION OF THE UNTANNED HUMAN SKIN TO ULTRA-VIOLET RADIATION

By W. W. Coblentz, R. Stair, and J. M. Hogue

ABSTRACT

The spectral erythemic reaction of three persons exposed to equal amounts of homogeneous ultra-violet radiation, of various wave lengths, is described. The source of radiation was a standard vertical quartz mercury vapor lamp which has a series of intense conveniently spaced emission lines, extending from 248 to 365 mμ. These emission lines were separated by passage through the spectrometer exit slit, the jaws of which were dusted with anthracene, which, by fluorescence, indicated the accuracy of the isolation of the line under investigation.

The erythemal reaction and the radiometric measurements were made on the spectral line directly back of the exit slit. In the region of 250 mμ the spectral erythemic reaction was supplemented by exposures to the heterogeneous radiation from a mercury vapor lamp having a high selective emission in the resonance line at 253.7 mμ. Data are given on the reciprocity of intensity and time of exposure, and also on the relative spectral erythemic reaction in the range of wave lengths extending from 245 to 315 mμ.

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I. INTRODUCTION

In connection with an investigation, now in progress, of methods of measuring the dosage of ultra-violet radiation used for healing purposes, the need has arisen for exact numerical data on the spectral erythemic reaction of the untanned human skin to equal amounts of ultra-violet radiation of various wave lengths. Manifestly the amount of ultra-violet radiation that can be applied, without producing a burn, depends upon the tolerance of the skin. This tolerance is widely different for different persons, and widely different even for the same person, depending upon the amount of moisture on the skin.

Hence, the erythemic response is commonly used as an indicator of the amount of ultra-violet radiation that can be applied at any one time. Furthermore, in view of the limitations imposed by skin tolerance, it is highly probable that any unit of dosage, or any inanimate dosage meter that may be adopted will have to take this physiological effect into consideration. This is a safe and logical procedure, even though the spectral erythemic reaction may not be closely related with the spectral reaction in curing disease; for example, rickets.

Hence, in an investigation, now in progress, of the amount of ultra-violet, useful for healing purposes, that is emitted by various sources,

the radiometric measurements are supplemented by observations of the time and intensity required to produce a minimum perceptible erythema, using measured amounts of ultra-violet from the unknown heterogeneous source of radiation undergoing tests and from the standard source of homogeneous radiation of maximum erythemogenic effectiveness, which, for practical purposes, is the emission line of mercury at 296.7 mμ (1).[1]

Previous determinations of the erythemic response of the human skin when exposed to ultra-violet radiation of different wave lengths were made by Hausser and Vahle (3) and more recently by Luckiesh (4) and his collaborators. In their determination of the energy required to produce a minimum perceptible erythema, Hausser and Vahle exposed the arm to single emission lines, which passed through a slit (3 cm long) in a cardboard attached to the arm. Based upon their preliminary observations of the approximate magnitude of the erythemal dose for each wave length, by making the exposure through the whole length of the slit, then through two-thirds and finally through one-third of the length, for different time intervals (three exposures with each line), the exposure time for producing a distinctly perceptible erythema was determined.

Instead of using isolated spectral lines, Luckiesh (4) and his collaborators exposed small areas of the subject's back to the total radiation from a quartz mercury arc lamp, shining through filters that shut off successively increasing wave lengths of ultra-violet radiation, and noting the dosage necessary to produce a minimum perceptible erythema. For this purpose the time was varied so that the shortest exposure gave no visible results, and the longest exposure produced a definite erythema, as observed after a lapse of approximately 24 hours.

II. EXPERIMENTAL PROCEDURE

In the present investigation spectral lines (isolated by means of a large quartz monochromator (5) having plano-convex lenses 6 cm diameter, 18 cm focal length) were used as stimuli, and the time of exposure to produce a minimum perceptible erythema (one that lasted less than 24 hours) was determined. As found by others, the difficulty lies in defining the minimum perceptible erythema, especially the highly transitory erythema produced by wave lengths less than 270 mμ which, for a weak dosage, increases to a maximum redness and then disappears in the course of 2 to 5 hours. In contrast, the erythema produced by the more deeply penetrating radiation, of wave lengths 302 and 313 mμ, does not begin to be visible until about 4 or 5 hours after exposure. Form this it can readily be seen that on exposure to heterogeneous ultra-violet radiation the erythemal effect of the shortest rays may be waning by the time the erythema, caused by the longer ultra-violet rays, is beginning to be perceptible.

The source of ultra-violet radiation used in the present work was a vertical quartz mercury vapor lamp, operated on a constant voltage (65 volts, 4 amperes in the burner), under which condition the intensities of the spectral lines, measured at different times with a linear thermopile (6) calibrated in absolute value, (7) were constant to 5 per cent.

[1] Figures in parentheses, here and throughout the text, indicate references given in the bibliography at the end of this paper.

The exit slit (of metal 0.1 mm in thickness, with beveled edges turned away from the incident light) (8), was mounted upon a movable support which, after focusing upon the desired spectral line, was securely attached to the spectrometer arm.

To facilitate setting on a spectral line the slit was given a thin coat of turpentine upon which was dusted a thin deposit of anthracene, which was then rubbed smooth. Starting with the slit closed, this method of applying the fluorescent material produces a sharp knife-edge which, on opening the slit (0.3 mm wide, 10 mm long), permits an accurate isolation of closely adjoining emission lines.

The arm of the subject, to be exposed to ultra-violet radiation, rested upon a movable support directly back of, and within less than 0.3 mm from the front surface of the exit slit. The difference in focus of the radiation incident upon the exit slit, and incident upon the skin directly back of the slit, was therefore negligible. By moving the arm support laterally, different parts of the arm (usually at intervals of 4 to 6 mm) could be exposed to radiation. Tests were made on the inner forearm and on the inside upper arm. The three subjects examined were of the white race, dark haired, and of average skin pigmentation.

In practice the exit slit was adjusted to transmit a given emission line (for example, 297 mμ) and a series of irradiation exposures was made, ranging from 1.5, 1.75, 2.0, 2.25, 2.50, and 3.0 minutes. From such a series of exposures the time for producing a minimum perceptible erythema (1.75, 2.0, and 2.5 minutes respectively, for the three observers, in the winter time when the skin was dry) was easily established. In the summer time, when the skin was moist and the time of exposure for producing a minimum perceptible erythema was only about one-half to two-thirds as long, the intervals between the successive exposures was reduced to 10 seconds instead of 15 seconds formerly used.

When making irradiation tests in the region of 254 mμ, where the observations of the erythemic reaction are in disagreement with previous experimenters, check exposures were made on the 297 mμ line alongside with the exposures to the emission line (for example, 248 mμ) under observation. Since the minimum perceptible erythema for the 297 mμ line was produced in the usual time (1.75 minutes; 2 minutes produced an erythema lasting 2 days for W. W. C) it was assumed that this disagreement is real. However, it was realized, at the time (2) that the estimation of a minimum perceptible erythema, which is so transitory as that produced by wave lengths less than 270 mμ, is subject to an appreciable error, resulting from overexposure. Attention was called to this fact in the preliminary paper (2) on this subject.

In the meantime, the demand having arisen for more accurate data on the spectral erythemic response in the region of 250 mμ, tests were made with a so-called "cold quartz" mercury vapor lamp (Geissler tube discharge in a quartz tube) in which 95 to 98 per cent of the total ultra-violet erythemogenic radiation of wave lengths less than and including the 313 mμ line is contained in the resonance line at 253.7 mμ.

Using the heterogeneous radiation from such a lamp, it is possible to expose wider areas than 0.3 to 0.4 mm (which was the maximum

width in the spectrally isolated homogeneous radiation) and to note the appearance of a faint reddening of the skin that would continue to be visible for 5 to 10 hours, as probably would be done by a physician, using ultra-violet radiation for therapeutic purposes.

III. THE RECIPROCITY LAW

According to Luckiesh (9) the reciprocity law holds for biological effectiveness over a wide range of exposures. In the production of a minimum perceptible erythema the reciprocity law was found to hold satisfactorily over the entire range of three hours investigated.

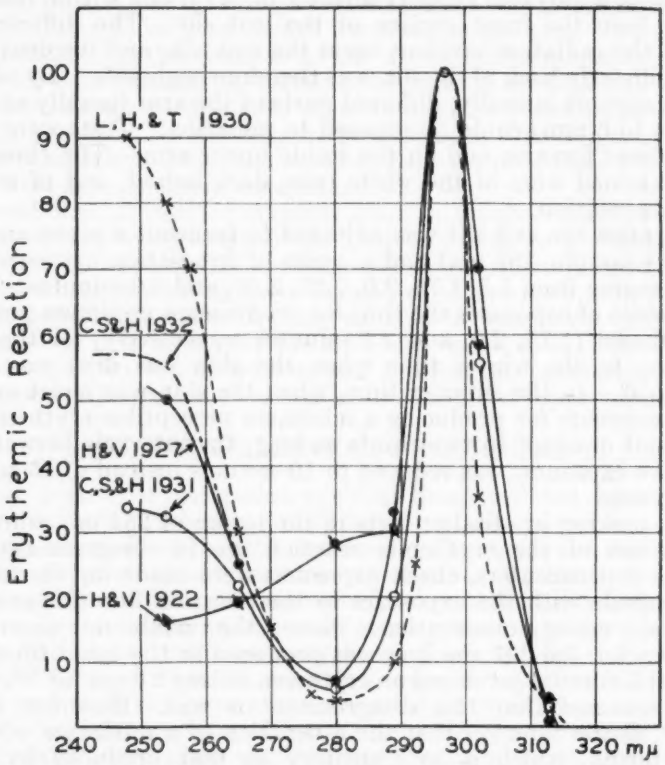

FIGURE 1.—*Relative spectral erythemic reaction of the human skin to equal amounts of radiant energy at various wave lengths; H. and V., Hausser and Vahle; L. H. and T., Luckiesh, Holladay and Taylor; C. S. and H., Coblentz, Stair, and Hogue*

In the present experiments the intensity of the emission line at 297 mμ was reduced by one-half, and by one-fourth, by means of glass filters, and the corresponding time of exposure was doubled and quadrupled. Within the experimental errors involved in making the test, the erythema produced by using one-fourth of the unit intensity and exposing for four times the unit time, was not appreciably different from that produced by exposing the subject to unit intensity (430 microwatts per cm^2) for the unit time (2 minutes for R. S.) required to produce a minimum perceptible erythema.

From the foregoing tests, it appears that the reciprocal relation of intensity and time of exposure (the lower the intensity the longer the exposure, and vice versa) is correct for the intensities and corresponding times of exposure that will be encountered in ultra-violet radiation therapy.

IV. THE SPECTRAL ERYTHEMIC REACTION

As illustrated in Figure 1, the wave length range of the erythemogenic rays begins at about 315 mμ, and extends to an undetermined wave length shorter than 240 mμ. The erythemic response curve rises steeply to a maximum at 297 mμ, descends less steeply to a minimum at about 280 mμ, then rises to a less intense maximum in the region of 250 mμ. Considering the difficulties, these magnitudes are in good agreement throughout. However, as already explained, the disagreement of the spectral response curve in the region of 250 mμ arises in part from the method of defining the minimum perceptible erythema, which is very transitory for short-wave lengths. This appears to be of minor importance in view of the increased practice of covering artificial light sources with a glass that intercepts ultra-violet radiation of wave lengths less than 280 mμ, thus reducing the erythemogenic range of wave lengths to agree more nearly with that of the sun.

From direct experiments on the production of a minimum perceptible erythema using measured amounts of heterogeneous ultra-violet radiation from various sources, including (*a*) the so-called "cold quartz" lamp (low vapor pressure mercury arc, in which practically all the erythemogenic radiation is contained in the emission line at 253.7 mμ), (*b*) the high-amperage, high vapor-pressure, quartz mercury-arc lamp, and (*c*) the sun, it is found that the spectral erythemic response, for wave lengths less than 280 mμ, is represented by the curve (dots and dashes) marked "C. S. & H. 1932" depicted in Figure 1. In the region of 250 mμ, this curve is slightly higher than the average value of the various observers.

In their investigations now in progress, involving the determination of the rubescence curve, which is the product of the spectral energy distribution of the source and the spectral erythemic response curve of the skin (analogous to the luminosity curve, which is the product of the spectral energy curve of the source and the visibility of the eye) the writers have adopted, as standard, the spectral erythemic response data, given in Table 1, in which the wave length of maximum erythemic reaction is taken at the emission line of mercury at 296.7 mμ (2967 A). Excepting at 254 mμ these data are practically the average of the various observers.

TABLE 1.—*The relative spectral erythemic reaction of the untanned human skin to equal amounts of radiant energy, averaged (excepting at 254 mμ) from the measurements of Hausser and Vahle (spectrally homogeneous radiation 1922 and 1927), of Luckiesh, Holladay, and Taylor (filter method, 1930) and of Coblentz, Stair, and Hogue, using (in 1931) homogeneous radiation, and (in 1932) heterogeneous radiation from a mercury vapor lamp, having 98 per cent of the erythemogenic radiation in the 254 mμ line*

Wave length	Erythemic response
mμ	
315	0.00
313	.03
310	.11
305	.33
302	.55
300	.82
297	1.00
295	.95
290	.26
289	.22
285	.09
280	.06
275	.07
270	.13
265	.25
260	.42
258	.48
254	.55
248	.57
245	.57
240	.56

V. CONCLUSION

The erythemogenic power of ultra-violet radiation depends upon the intensity of the rays and upon the susceptibility of the skin to different wave lengths. But unlike the spectral sensibility curve of the eye which is perceptibly different for different persons, from the limited data available it appears that the spectral erythemic response curve of the human skin is practically the same for different persons, in spite of the fact that the total energy required to produce an erythema is markedly different.

One difficulty in devising a suitable dosage meter is owing to the fact that a long overexposure to radiation at 254 mμ produces only a superficial burn, whereas a slight overexposure to the more deeply penetrating radiation of wave length 313 mμ produces a painful blister. For example, in one case it was found that an exposure to the wave length 313 mμ for 14 minutes produced a barely perceptible erythema (estimated exposure 15 minutes); 16 minutes was somewhat longer than required for a minimum perceptible erythema; and an exposure of 18 minutes produced a painful blister.

On the basis of the limited number of subjects tested in this work, the total energy required to produce a minimum perceptible erythema upon 1 cm^2 of untanned skin, using homogeneous radiation of wave length 297 mμ (the wave length of maximum of erythemic susceptibility) in the winter time, when the humidity is low and skin is dry, is of the order of 500,000 ergs. The actual values for the three observers were, respectively, 452, 516, and 645 kiloergs per cm^2.

During the summer time (high humidity, skin moist) the values, for these three observers, were respectively 221, 309, and 190 kiloergs per cm^2, or an average of about 240 kiloergs. In other words, the average time of exposure for producing a minimum perceptible erythema was reduced to one-half the winter value. The most conspicuous change was on J. M. H., whose exposure time was reduced to one-third the winter value.

When one considers the ever-increasing number of ultra-violet radiators sold for healing purposes, in some of which about 97 per cent of the total erythemogenic radiation, of wave lengths 200 to 315 $m\mu$ is contained in the highly germicidal but nonpenetrating rays at 254 $m\mu$ (the resonance line in a so-called "cold" quartz mercury lamp), while other lamps contain practically no ultra-violet radiation of wave lengths shorter than 300 $m\mu$, but emit longer wave lengths that are more penetrating and more potent in causing burns, the urgent need of a means of standardization of the dosage seems apparent.

In a subsequent paper data will be presented correlating the radiometric "dosage" measurements and the erythemal reaction of the standard sources of ultra-violet radiation now available for therapeutic purposes, as outlined in a preceding paper (1) in which a practical application was made of the herein-described data.

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